PD
539.7
A693
V. 5, No. 3

REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

July 1962

● VOLUME 5

● NUMBER 3

TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

The four journals published in this series are:

Nuclear Safety, Wm. B. Cottrell, W. H. Jordan, and associates, Oak Ridge National Laboratory

Power Reactor Technology, W. H. Zinn and J. R. Dietrich, General Nuclear Engineering Corporation

Reactor Materials, R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Each journal may be purchased ($2.00 per year for subscription and individual issues $0.55) from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. See back cover for remittance instructions and foreign postage requirements.

The views expressed in this publication do not necessarily represent those of the United States Atomic Energy Commission, its divisions or offices, or of any Commission advisory committee or contractor.

Availability of Reports Cited in This Review

Unclassified AEC reports are available for inspection at AEC depository libraries and are sold by the Office of Technical Services, Department of Commerce, Washington 25, D. C. Some of the reports cited are not available owing to their preliminary nature; however, the information contained in them will eventually be made available in formal progress or topical reports.

Unclassified reports issued by other Government agencies or private organizations should be requested from the originator.

Unclassified British and Canadian reports may be inspected at AEC depository libraries. British reports are sold by the British Information Service, 45 Rockefeller Plaza, New York, N. Y.; Canadian reports (AECL series) are sold by the Scientific Document Distribution Office, Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Classified U. S. and foreign reports identified in this journal as Classified may be purchased by properly cleared Access Permit Holders from the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 1001, Oak Ridge, Tenn. Such reports may be inspected at classified AEC depository libraries.

REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

● JULY 1962
● VOLUME 5
● NUMBER 3

Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., I. G. Dillon, P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

Contents

Foreword

I COMMERCIAL ASPECTS OF FUEL PROCESSING 1

Fuel-Processing Plans 1
Fuel Cycles 2
References 3

II RESEARCH AND DEVELOPMENT ON AQUEOUS PROCESSING 4

Preparation for Fuel Processing 4
Solvent-Extraction Processes 10
Process Instrumentation 13
Design and Operation of Plant Equipment 14
Corrosion 15
References 20

III RESEARCH AND DEVELOPMENT ON NONAQUEOUS PROCESSING . . . 22

Volatility Processes 22
Pyrometallurgical Processes 27
Other Nonaqueous Processes 34
References 39

IV WASTE DISPOSAL 41

Evaluation of Containers for Sea Disposal 41
Land Burial: Operating Experience . . . 42
Treatment of Liquid Wastes by Separation of Specific Isotopes 43
Conversion of High-Level-Activity Liquid Wastes to Solids 47
Final Disposal 54
Recovery of Fission-Product Isotopes . . 57
References 59

V PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS 61

Preparation of Uranium Dioxide 61
Preparation of U(IV) Nitrate Solutions . . . 63
Production of Uranium Tetrafluoride by Reduction of Uranium Hexafluoride 63
Production of Plutonium Metal 64
Recovery of Plutonium from Scrap Materials 67
Plutonium Chemistry and Technology . . . 69
References 70

Issued quarterly by the U. S. Atomic Energy Commission. Funds for printing this publication approved by the Director of the Bureau of the Budget on November 1, 1960.

Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

The Atomic Energy Commission (AEC) has announced that it plans to enter into negotiation with the Davison Chemical Company, Baltimore, Md. (a Division of W. R. Grace & Company), with the object of developing a mutually satisfactory arrangement for the processing of irradiated fuel elements from nuclear power reactors.[1] The proposed Davison plant would be the first such privately owned facility in the nation. Processing facilities exist at AEC installations for processing fuels from production reactors but not for fuel from power reactors. The two fuels are dissimilar.

Davison would set up a wholly owned subsidiary, to be known as Nuclear Fuel Services, Inc. Davison's plan is the result of studies by the Industrial Reprocessing Group (IRG), comprised of Davison and five power companies, Consolidated Edison, Commonwealth Edison, Detroit Edison, Yankee Atomic Electric, and Northern States Power.

Davison has made its offer contingent also upon AEC's willingness to furnish during a five-year period a portion of spent fuel from its own reactors. The guaranteed load requested from AEC by Davison is estimated to be within the amount of fuels to be generated in AEC nonproduction operations. The Commission expects to be able to furnish a portion of its spent fuel to help meet the initial requirements of the plant and, in addition, be in a position to provide an equivalent quantity of irradiated fuel to another processor should a qualified processor apply.

Davison has advised the Commission's Division of Licensing and Regulation of its intent to proceed with an application for a license to design, construct, and operate a processing plant. Plans are to have the plant ready for operation by 1965.

Davison has contracted with Bechtel Corp. to provide the engineering detail necessary for the license application. Bechtel has also been performing engineering studies of two sites for the plant, one of which is the New York State proposed nuclear service center.[2]

The proposed Davison plant would have a nominal capacity of 1 ton per day or 200 tons per year and would be capable of processing, at varying throughput rates, essentially all the current designs of fuel elements except the graphite-matrix variety. The plant would contain: (1) a fuel-receiving and -storage area, including facilities for shipping-cask decontamination, maintenance, and storage and for canning ruptured fuel elements; (2) a fuel inspection, disassembly, and chopping area; (3) an area for dissolving spent fuel elements; and (4) solvent-extraction facilities.[3]

The solvent-extraction process would include a partition cycle for uranium-plutonium and thorium-uranium; second thorium, uranium, and plutonium cycles; third uranium cycle; plutonium ion-exchange cleanup; uranium and plutonium product handling; solvent cleanup; acid recovery; and waste handling and storage.[3]

Meanwhile two large U. S. power reactors are nearing the time when the first spent fuel will be ready for processing. The entire first core of the Yankee reactor and a portion of the first core of the Dresden reactor are expected to be cooled and ready for shipment in the fall of 1962. In view of the Davison commitment for a privately owned plant, the processing plans for the Yankee and Dresden fuels are somewhat uncertain. Shipment to the AEC's Savannah River processing plant is one possibility. However, the installation of facilities

for the processing of power-reactor fuels at Savannah River has been delayed because the construction of a privately owned plant would make this expenditure unnecessary. In the interim the irradiated fuel would have to be stored. Another possibility might be the construction of a storage facility to hold shipments at the site of the future Davison plant. Presumably the shippers could hold spent fuel at the reactor sites until storage is available. Storage capability is available at the Dresden site for the first 96 elements to come out of the reactor, but storage capacity is limited.

A complicating factor in the disposition of the first spent fuel from these two power reactors concerns the expiration on June 30, 1963, of the AEC's guaranteed plutonium purchase price of $30 per gram. If the fuel is not received in time to complete the processing (hypothetically) by that date, it would not qualify for the $30 price, under existing commitments.

A 75-ton cask, to cost $500,000, has been designed for shipment of the Yankee reactor fuel, and a special railway car will be built to carry the cask. Final approval of the cask design is awaiting AEC's formal adoption of regulatory standards governing cask design. Rail transportation rates for shipments of this kind have yet to be resolved.[4]

European fuel-processing projects include the Eurochemic plant under construction for processing slightly enriched fuel, sponsored by the European Nuclear Energy Agency, and the EUREX plant that Italy proposes to build for processing highly enriched fuel. Completion of these two plants would make it possible for reactor operators in Europe to avoid the complications of shipping irradiated fuel by sea for processing in the United States. Financial support for both projects is being sought from Euratom. The proposed Euratom budget lists $5 million for fuels-processing projects—$2 million of it for completing the Eurochemic facility and $3 million for participation in a project for processing highly enriched fuel, presumably the EUREX project.[4–6]

Fuel Cycles

The manner in which nuclear fuels are used and recycled in nuclear reactors can have a very great effect on the amount of energy released per pound of nuclear fuel. This subject and its effect on the long-term utilization of uranium and thorium are discussed in a report prepared by the AEC's Division of Operations Analysis and Forecasting.[7] Because the losses that occur in fuel processing have an important bearing on the energy available from nuclear fuel, portions of the report are summarized here.

The amount of heat made available per pound of nuclear fuel depends on the extent to which new fissile isotopes are created as the fuel is being consumed, the degree to which the fuel is recycled in reactors, and the irrecoverable losses of nuclear material which occur in the various processing steps in the preparation and recycling of fuel. Breeder reactors, which produce more fissile material than they consume, offer the possibility of the greatest utilization of uranium and thorium. Even in nonbreeders, however, the utilization of nuclear material may be improved by the recycle, with fertile material, of the plutonium or U^{233} that was produced in a previous cycle.

Recycle of plutonium and U^{235}, although improving fuel utilization and hence reducing fuel consumption costs, may entail additional costs due to handling and shielding problems associated with recycle material. The net effect may be an increase in cost if recycle is employed. Similarly, in the period when the technology is just being developed, breeder reactors may prove to be a more expensive way to produce electricity than by nonbreeder reactors.

The reference report[7] discusses a mathematical method for the quantitative measure-

Table I-1 UTILIZATION OF URANIUM[7]

Reactor type*	Processing losses per cycle, %	Utilization of uranium, %
Boiling-water reactor:		
With Pu recycle	0.4	1.6
Without Pu recycle	0.4	0.67
Pu used in separate burner reactor	0.4	0.94
Faster breeder with Pu recycle:		
Followed by fast burner	2	29.4
Followed by thermal burner	2	24.9

*Irradiation levels: Boiling-water reactor, 8800 Mwd/metric ton of uranium per cycle. Fast reactor, Pu region, 18,200 Mwd/metric ton of uranium plus plutonium; blanket region, 910 Mwd/metric ton of uranium.

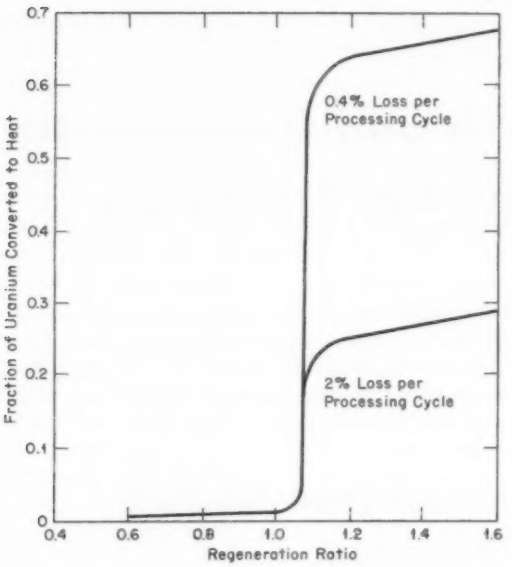

Fig. I-1 Utilization of uranium.[7]

ment of how utilization of uranium and thorium in nuclear reactors is affected by recycle and by losses outside the reactor. In this analysis, one starts with a fixed, large quantity of natural uranium (or thorium) which is used in nuclear reactors, and in such other facilities as a U^{235}-isotope enriching plant, chemical processing and fabrication plants, and others as are required, with repeated recycle and reuse of portions of the material until it is no longer possible to fuel a reactor and release any additional heat energy. Plutonium derived from the initial uranium can be used in whatever way is most advantageous. The fractional utilization of the uranium is then determined as the total number of fissions which have occurred in the system divided by the total number of uranium atoms in the initial fixed quantity.

In carrying out the calculations, a reactor with specified characteristics is operated for a chosen irradiation period, the fuel is discharged, and a new reactor fuel load is made up with any desired combination of uranium and plutonium at any desired enrichment derived from the initial stock or recovered from the irradiated fuel. Irrecoverable losses during chemical processing operations are assumed to be some specified fraction of the weight of material processed, per processing cycle.

For the uranium-plutonium system, fissile materials are taken to be U^{235}, Pu^{239}, and Pu^{241}, and fertile materials are U^{238} and Pu^{240}. The isotopes U^{236} and Pu^{242} are regarded as neither fissile nor fertile and are regarded as lost from the system.

Using the mathematical expressions derived from this analysis and physics data obtained from the literature, the fractional utilization of uranium was calculated as shown in Table I-1. To extend the results to reactors with different conversion ratios and different losses in the processing cycle, estimates were made of how the parameters would change. Typical results are shown in Fig. I-1. The data, although only approximate, are nevertheless useful in illustrating how strongly the heat output per unit of natural ore reserves can be affected by chemical processing losses, as well as conversion ratio.

References

1. AEC Negotiating with Davison Firm for Private Processing of Irradiated Fuel, AEC Press Release E-80, Mar. 15, 1962.
2. *Reactor Fuel Processing*, 4(4): (October 1961).
3. *Nucleonics*, 20(3): (March 1962).
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 9(2): (February 1962).
5. *Nucleonics*, 20(4): (April 1962).
6. *Reactor Fuel Processing*, 5(2): (April 1962).
7. D. W. Kuhn and R. D. Walton, Jr., Long Term Utilization of Uranium and Thorium, USAEC Report TID-13901, October 1961.

Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

According to current practice, uranium, plutonium, and other useful materials are recovered from spent nuclear fuels by dissolving the fuel elements in strong aqueous acids, extracting the desired products from the aqueous solution with organic solvents and effecting their separation from undesired materials and each other thereby, and, finally, purifying by ion exchange or adsorption. Preliminary separation of cladding or structural components of the fuel assemblies by chemical or mechanical means may be used to simplify subsequent processing. Because of the importance of aqueous processing techniques in present nuclear technology, research and development studies are continually carried on to improve present processes and to adapt them to the treatment of newer and more complex fuel materials.

Preparation for Fuel Processing

Current studies of methods of fuel preparation largely involve chopping clad uranium

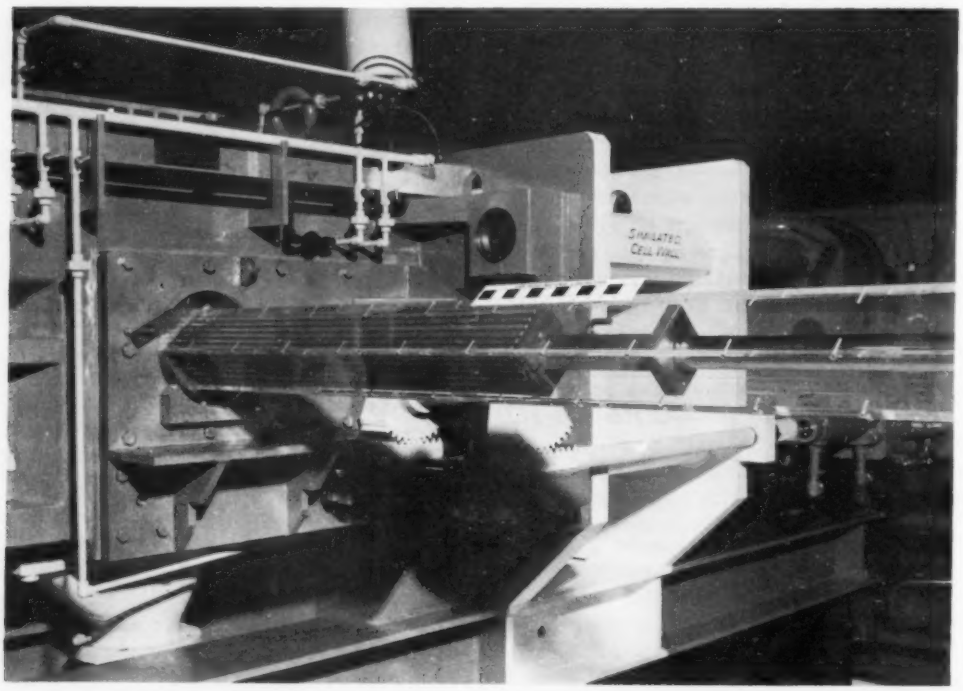

Fig. II-1 Pusher arm positioning fuel assembly against stop.[1]

oxide fuels, dissolving zirconium and stainless steel, and leaching uranium from graphite and ceramic compositions.

Mechanical Processing Methods

Finney reports[1] further on the Oak Ridge shear-leach program[2] to determine the economics and technological feasibility of continuously leaching core material (urania or urania-thoria mixtures) from relatively short sections (1 in. long) of fuel elements produced by shearing. The 250-ton prototype shear consists primarily of a remotely operable shear powered by a hydraulic oil system and a hydraulic or pneumatic feed mechanism. The sequence of operating the shear follows: a fuel assembly is picked up with a crane and inserted into the fuel-element envelope by means of the loading arm. The pusher arm is moved into position where it pushes the fuel assembly into the shear against a stop, initially and after each cut is made (see Fig. II-1); a step-shaped movable blade shears the fuel assembly into short sections ($\frac{1}{4}$ to 1 in. long). Both the stop and step blade are mounted on the ram as shown in Fig. II-2. The fuel assembly is held during shearing by an inner and outer gag and by the fixed blade. After the ram has made a complete stroke (forward and backward), the gags are released so that the fuel assembly can be moved forward against the stop for the next cut.

In the initial shear operation on porcelain-filled stainless-steel tubes, Finney[3] reported that it was difficult to hold the assembly securely while advancing to the stop for the next cut, especially since it is desirable to shear within 1 in. of the end. The cuts have been made across the diagonal of the assembly leaving a crushed end that assumes an approximate 30° slope. This angle increases to 45° when sheared near or at the double-row ferrule bank as shown in Fig. II-3. This changing shape has caused difficulty with the gag, and two new approaches will be tried:

1. Spring loading the inner gag so that it will retract easily when contacted by the fuel assembly and thus conform it to the changing shape

2. Shearing into the flat side of the assembly to minimize deformation of the sheared face

It was reported that a Squarkeen No. 3 (American Knife Co.) stepped moving blade having a Rockwell C hardness of about 59 has made 800 cuts on simulated fuel assemblies with no sign of wear.

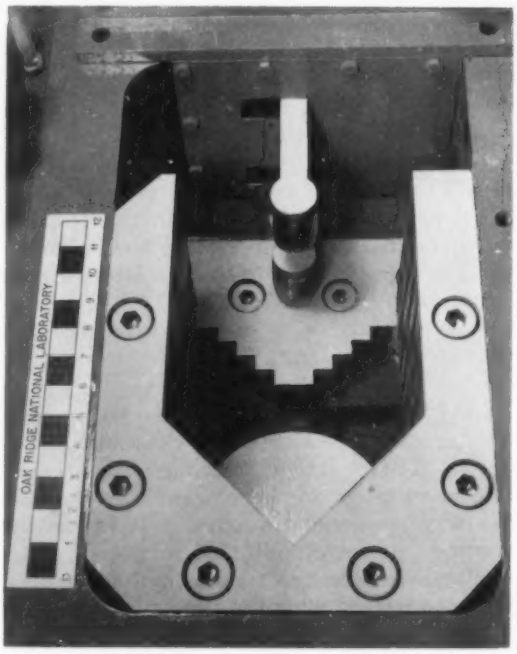

Fig. II-2 View of step blade, stop, gag arms, and fixed blade, with gags and face plate removed.[1]

Chemical Removal of Jacket Materials

Ewing and others at Battelle have reported[4] in detail on work previously summarized by Oak Ridge[2] on the effect of irradiation in dissolving the stainless-steel cladding from Consolidated Edison reactor type thoria-urania pellets in sulfuric acid and in nitric-hydrochloric acid mixtures. Both detrimental and beneficial effects were observed. Losses of both fissile and fertile materials to decladding solutions increased with increasing burnup, only very slightly with sulfuric acid decladding, but significantly (to the order of several per cent) with nitric-hydrochloric acid decladding. Dissolution of the thoria-urania core, however, which is accomplished only with difficulty on the unirradiated fuel (in 13M nitric acid containing 0.04M sodium fluoride and 0.1M aluminum nitrate), is rapidly effected on high-burnup fuel. The observed losses to the decladding solutions in the Battelle work are summarized

in Table II-1. Other work at Oak Ridge National Laboratory (ORNL) on unirradiated fuel had indicated that losses tended to decrease with decreasing urania content.

Shattering or fragmentation had occurred in all the irradiated specimens, and the resulting increase in surface area might be expected to increase the uranium loss. Qualitatively, shattering increased with increasing burnup. However, even at 22,000 Mwd/ton, shattering was not markedly greater than at 10,000 Mwd/ton, and no degradation to extreme fines was apparent.

Gens,[5] in a review of niobium chemistry, notes that no dissolution method for niobium metal has yet been found to be compatible with present radiochemical plant technology, since all aqueous acid reagents that attack niobium rapidly are too corrosive for containment in readily available construction materials. Niobium dissolves rapidly in mixed nitric-hydrofluoric acids and probably will dissolve in hydrofluoric acid–hydrogen peroxide mixtures. It can also be dissolved in sulfuric acid that is more concentrated than 14 molar. High dissolution rates have also been observed in alcoholic hydrogen chloride or alcoholic mercuric chloride. Anhydrous conditions must be maintained with the hydrogen chloride reagent since the presence of water results in the formation of an insoluble deposit on the metal.

Dissolution of Fuel Cores

Several years ago, when it was planned to process certain low-enrichment power-reactor fuels in the Hanford Redox plant, considerable work was done at Hanford to produce low-acidity dissolver solutions from fuels of various types for methyl isobutyl ketone extraction. Hanford work on uranium–3 per cent molybdenum alloy fuel (as planned for the Piqua reactor) has been described previously.[6] In a recent article Schulz[7] gives two additional flow sheets for dissolving such an alloy using strong nitric acid. In the first scheme, precipitated molybdic oxide is dissolved with caustic in the centrifuge, and the resulting molybdate solution

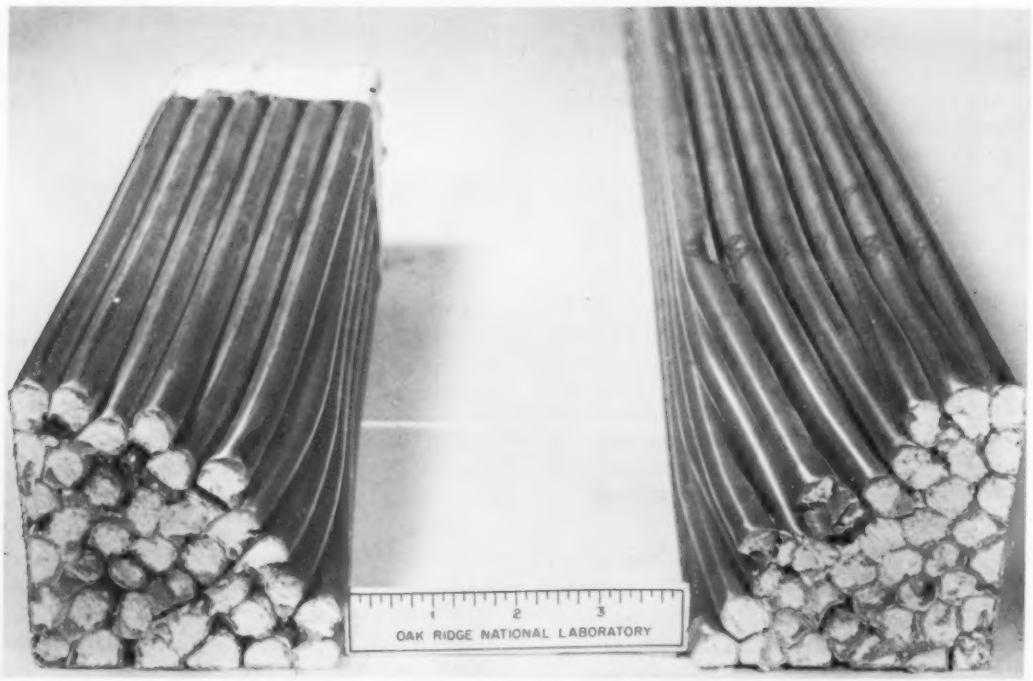

Fig. II-3 Comparison of bundle shape using a stepped movable blade to shear across the diagonal of a porcelain-filled ORNL Mark I fuel assembly.[3]

is sent to waste. Residual sodium uranate is then dissolved in nitric acid. Excess acid in the supernatant and washings is destroyed with formaldehyde to yield a slightly acid uranyl nitrate feed. According to the second scheme, precipitation of molybdenum is prevented by dissolving the alloy in strong acid in the presence of ferric nitrate, which is presumed to form a soluble iron-molybdenum complex ion. In this case the excess acid is neutralized with dibasic aluminum nitrate. The results of low-level solvent-extraction studies are also given.

Table II-1 URANIUM AND THORIUM LOSSES IN DECLADDING STAINLESS-STEEL-CLAD URANIA-THORIA FUEL

[Cladding Material: Type 304ELC Stainless Steel (20 mils)]

Specimen group	UO_2 in fuel initially, %	Burnup range, Mwd/ton	In decladding 3 hr with 6*M* sulfuric acid			In decladding 1 to 1.5 hr with 5*M* nitric acid–2*M* hydrochloric acid mixture		
			No. of samples	Uranium lost, %	Thorium lost, %	No. of samples	Uranium lost, %	Thorium lost, %
A	9.5	0	1	0.008	0.006	2	0.04–0.05	0.005–0.014
B	9.5	700–1000	2	0.05–0.12	0.04–0.11	3	0.16–0.30	0.08–0.20
C	6.5	7,000–16,000	3	0.03–0.15	0.03–0.30	1	0.85	0.09
D	4.5	13,000–22,000	2	0.01–0.14	0.03–0.04	4	1.3–2.6	0.05–0.09

Certain fuel elements, called "spike" elements, in the Plutonium Recycle Test Reactor (PRTR) at Hanford consist of an alloy of aluminum with low percentages of plutonium and nickel. Dissolution rates for this alloy in nitric acid–mercuric nitrate solutions are very high at nitric acid concentrations up to 4*M*; at higher nitric acid concentrations, surface activation does not occur and dissolution rates are equivalent to those obtained in nitric acid alone. In attempts to obtain intermediate dissolution rates, dissolvents containing 6*M* to 8*M* HNO_3, 0.002*M* to 0.05*M* $Hg(NO_3)_2$, and 0.03*M* ammonium fluoride to promote activation were tried.[8,9] Activation at the lower mercuric nitrate concentrations (0.005*M* or greater) was reproducible, but the initial dissolution rates were still greater than desired for handling a full charge of elements in the Redox dissolver. It was found that some control of the dissolving rate in these solutions could be obtained by having nickel ion present at low concentrations. Dissolution rates about one-third those observed in the absence of nickel were obtained when the dissolvent was 0.02*M* to 0.03*M* in nickel nitrate.

Process studies conducted at the Idaho Chemical Processing Plant on the reaction of molten lead chloride with zirconium-uranium alloys, to convert the uranium to a form suitable for solvent extraction, were described previously.[10] More recent studies show that uranium dioxide may be reacted rapidly with chlorine, in a lead chloride medium and in the presence of copper or iron, to produce a melt from which uranium can be recovered similarly.[11]

Total Dissolution of Metallic Fuel Materials

Dissolution of Zirconium-Rich Fuels. Gens[12] has recently summarized laboratory studies at Oak Ridge on the dissolution of uranium–zirconium hydride TRIGA fuel in ammonium fluoride and hydrogen peroxide. The resulting process flow sheet has been discussed previously.[13] Aluminum cladding and end pieces are dissolved in caustic nitrate, and graphite plugs are disintegrated with a mixture of fuming nitric and sulfuric acids. A somewhat modified flow sheet, shown in Fig. II-4, was used at Oak Ridge in the treatment of a full-size unirradiated TRIGA assembly.[14] Dissolution was slow because of the massive nature of the zirconium alloy slug. To simplify the process, it was suggested that in future work a preliminary mechanical treatment, consisting of cutting the aluminum cladding near each end of the slug, be used to remove the graphite pieces, samarium poison disks, and aluminum end fittings.

At Oak Ridge, studies are also being made of the continuous dissolution of Zircaloy in ammonium fluoride solutions that are modified by the addition of ammonium nitrate and hydrogen peroxide to permit complete dissolution of al-

loys containing more uranium than can be dissolved in ammonium fluozirconate solutions in the tetravalent state.[15] In a series of runs in a 2-in.-diameter dissolver, steady-state conditions were achieved with 6*M* to 6.5*M* ammonium fluoride containing either 1.0*M* ammonium nitrate or 0.1*M* hydrogen peroxide, or both. Dissolution rates were of the order of 4 to 6 mg/(cm^2)(min). Similar dissolution rates were obtained in scaled-up tests[1] using a 6-in.-diameter dissolver, from which a dissolver product stream containing 0.7*M* to 0.9*M* zirconium was obtained. Best operation was secured by withdrawing the ammoniacal overhead condensate, which was replaced by an equal volume of water, and by feeding the dissolvent at the top while removing the product from the bottom of the dissolver through a jackleg.

Adaptation of the hydrofluoric acid process for dissolving Zircaloy-uranium alloys is also being developed. At the Idaho Chemical Processing Plant (ICPP), in attempting to dissolve a 3 per cent uranium–Zircaloy-2 alloy in 10*M* hydrofluoric acid, the addition of 0.1*M* chromium trioxide produced a dissolver product equivalent in uranium concentration to a 2 per cent uranium alloy fuel.[16] Product of higher uranium concentration was obtained with 5*M* hydrochloric acid and no oxidant.

Since corrosive halides are normally required to dissolve zirconium-rich alloys, there have been continued attempts to use nitrate or other systems, for which stainless steel is suitable, to attack zirconium fuel materials. Bomar[17] at ICPP has reported on recent studies of electrolytic oxidation of Zircaloy-2 by nitrate solutions. As in other studies, only a portion (about 15 per cent) of the zirconium was dissolved in nitric acid, but the metallic plates were completely disintegrated and the undissolved zirconium was deposited as a fine black sludge. Sodium and aluminum nitrate solutions were also successfully used as electrolytes, although zirconium was not appreciably dissolved in the sodium nitrate solution. Rates of attack in sodium nitrate solution were as high as in nitric acid [of the order of 5 mg/(cm^2)(min)]. With a Zircaloy alloy containing a few per cent uranium, 6 to 28 per cent of the uranium remained with the sludge. In studies at the Savannah River Laboratory on the electrolytic disintegration[18] of Zircaloy-2, it was determined that the current utilization remained about constant at 1.0 ± 0.1 g/amp-hr over a range of nitric acid concentrations from 1*M* to 10*M*. In a 5000-amp pilot-plant dissolver test, about 250 lb of solid Zircaloy plates were disintegrated in 4.5*M* nitric acid in three batches, leaving a 20 per cent heel. The rate of attack exceeded 2.5 lb/hr. It was necessary to use a 100-lb weight on the plates to maintain good electrical contact, and, with such a weight, average current ranged from 1500 to 2000 amp at 13 volts, using an intermittent anode striker.

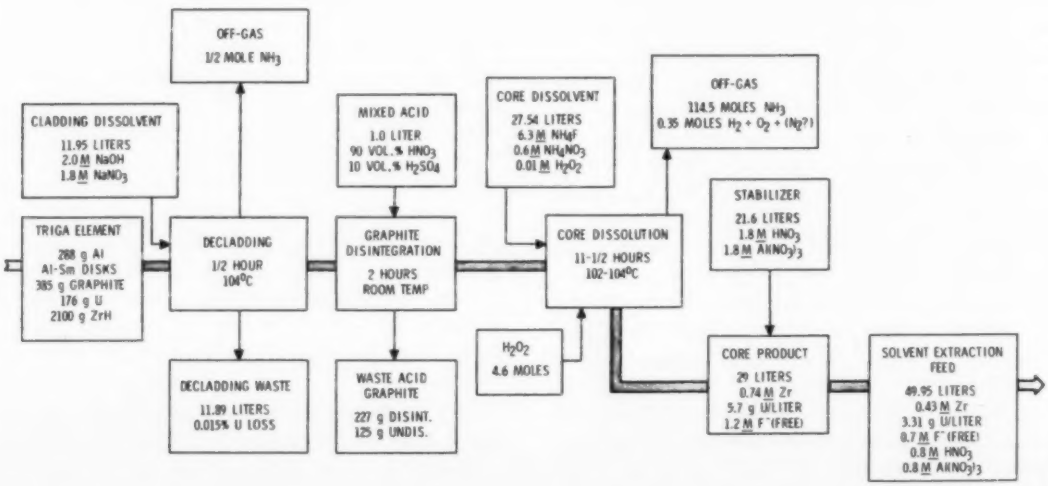

Fig. II-4 Aqueous processing of TRIGA fuel.[14]

Aylward,[19,20] in work at ICPP, has studied the electrolytic dissolution of zirconium in methanol containing hydrogen chloride. Solubility of zirconium in such a reagent is relatively high, at least 2.8*M*, presumably in the form of a chlorozirconium methoxide. At low overvoltages in the range in which overvoltage increases with the log of the current density, reaction rates are independent of hydrogen chloride concentration, and some of the zirconium separates as a finely divided alpha-zirconium residue. As the overvoltage is increased, the proportion of such a residue decreases until complete solution is attained in an overvoltage region (the electropolishing region—above about 0.6 volt) where the current density is independent of potential. This limiting current density decreases with increasing hydrogen chloride concentration and hence is controlled by mass transport.

Dissolution of Stainless-Steel Fuel Compositions. Nitric-hydrochloric acid dissolution of stainless steel–uranium oxide matrix fuels is a rapid and effective process but must be followed by removal of chloride from the solution (as by distillation) in order to prepare a suitable solvent-extraction feed. In studies at Oak Ridge[21] on dissolving such stainless-steel fuel which is used in the SM-1 remote power station reactor and which contains about 2 per cent silicon, voluminous quantities of insoluble silica are formed, which become highly hydrated during removal of chloride and plug the chloride stripping column. A 2-hr digestion of the silica-bearing solution at 90°C converted it to a form which was filterable and did not clog the distillation column. Treatment of the dissolver solution with gelatin, sometimes used in aluminum nitrate solution to aid silica coagulation, in this case produced a sticky, gelatinous precipitate.

The 5000-amp-capacity semiworks electrolytic dissolver[22] under investigation at Savannah River has been applied to the dissolution of mock fuel assemblies of stainless-steel pipe in 4.5*N* nitric acid.[18] When two 135-lb assemblies of ¼-in. pipe, 9 ft in length, were placed vertically in the dissolver basket so that only the lower 3 ft was submerged, it was possible to maintain an average current of 4000 amp, nominally equivalent to a rate of 0.1 ton of uranium dioxide fuel per day in this unit. However, arcing and overheating above the liquid occurred and burned holes in the stainless-steel portion of the anode basket as well as in the niobium liner in the lower portion. When bundles were cut to permit complete submergence and were weighted to improve contact, dissolving rates were almost as large, and there was no evidence of burning or overheating.

Nichrome cladding and matrix material, which was used in fuel for the Heat-Transfer Reactor Experiment (HTRE) tests by General Electric's Aircraft Nuclear Propulsion Department, can also be dissolved electrolytically in nitric acid. Aylward and Whitener, in reporting work at the ICPP,[23] note that the behavior of Nichrome can be predicted from knowledge of that of stainless steels and related alloys. A series of potential-current density measurements as functions of temperature and composition were made to determine conformance with predictions. Dissolution rates were found to decrease with increasing nitrate concentration and decreasing temperature.

Treatment of Nonmetallic Fuels

Graphite-Based and Carbide Fuels. For use in high-temperature reactors, particularly those which are gas-cooled, fuels composed of the carbides or oxides of uranium, thorium, or plutonium, as such or dispersed in graphite, are becoming of great interest. The fuel particles or the fuel mass may be coated with pyrolytic carbon, silicon carbide, alumina, or other high-temperature stable material. Recovery of nuclear materials from such fuels by aqueous reagents is hampered by the chemical inertness of the base materials and of the coatings. Mechanical size reduction to produce fine particles, combustion, or treatment with penetrating reagents such as fuming nitric acid may be necessary initial steps in processing.

Ferris and others[24] have recently summarized Oak Ridge work on the treatment of graphite-based fuels. Disintegration with 90 per cent nitric acid is effective in recovering 96 to 99 per cent of the uranium and most of the thorium present in either graphitized or ungraphitized fuels containing oxide or carbide particles, provided that the particles do not have a resistant coating. Multiple acid leaches may be required for high recovery. Fine grinding followed by leaching with 16*M* nitric acid, although not quite so effective in recovering uranium, may be used with coated particles, but the recovery of thorium requires the addition of a low con-

centration of fluoride to the acid. Combustion, followed by acid treatment of the combustion residue, can be used with all types of graphite-based fuels except those containing alumina- or beryllia-coated particles. Silicon carbide-coated materials require rough crushing before combustion, and some uranium may be retained in the residue.[25] It has also been reported that nitric acid leaching by continuous percolation of 90 per cent acid through a bed of $^3/_8$-in. graphite fuel cubes containing 3 per cent uranium is more efficient than a series of batch leaches[26] and yields low uranium loss. However, later tests in which the uranium-bearing graphite was crushed to −4 mesh yielded 0.6 to 1.5 per cent uranium loss at varying flow rates.[3]

Uranium carbide fuels may range in composition from the monocarbide containing excess uranium metal to the dicarbide containing excess carbon. Consequently, for aqueous processing, the hydrolytic behavior of the components and their mixtures becomes of significance. Bradley at Oak Ridge, in studies of the hydrolysis at 80°C of mixtures of the lower carbides and metal,[25] notes the general production of a relatively insoluble hydrous uranium oxide and marked variations in the composition of the gas produced. Hydrolysis of the monocarbide containing about 17 per cent uranium metal was slower than that of the monocarbide alone (presumably due to slow reaction of uranium metal) and yielded a mixture of methane with considerable hydrogen. Stoichiometric monocarbide produced a gas containing 85 per cent methane. A material whose over-all composition was that of the sesquicarbide, but which probably contained both dicarbide and uranium metal also, was hydrolyzed more slowly than the monocarbide and yielded a gas containing mostly hydrogen and ethane and higher hydrocarbons, with very little methane.

Beryllia- and Alumina-Based Fuels. Warren and others[27] at Oak Ridge have recently summarized work on dissolving ceramic pellets composed of uranium dioxide and either beryllia or alumina. Beryllia compositions are being used in several high-temperature gas-cooled reactors, such as the ML-1 and nuclear ramjet reactors. Most of the work described has been discussed previously in this Review.[28] Uranium may be completely leached from beryllia pellets containing 60 to 70 per cent uranium dioxide with boiling strong nitric acid or a dilute nitric-hydrochloric acid mixture (suitable also for the dissolution of Hastelloy X cladding), or the ceramic may be dissolved in nitric acid containing sulfuric or hydrofluoric acid. Fuels containing 95 per cent beryllia require strong sulfuric acid, or concentrated hydrofluoric acid with ammonium fluoride or fluoboric acid, for their dissolution.

Solvent-Extraction Processes

Decontamination and separation of the heavy-metal elements (thorium and elements of greater atomic number) present in aqueous solution are effectively accomplished by extraction with organic solvents. The most-used material for such extraction is tributyl phosphate (TBP), but other compounds are applicable to accomplish specific ends. Minor process improvements and modifications are being developed, and methods are being extended to accomplish new separations.

Tributyl Phosphate Processes for Uranium and Plutonium

In the extraction of uranium by diluted TBP, nitrate systems are generally preferred in part because organic-to-aqueous distribution ratios are most favorable. Certain other anions, such as sulfate, form uranium complexes that are relatively inextractable. In the refining of uranium ores, this is of particular importance since sulfuric acid leaching of the ore is a frequent initial step in uranium recovery. Sulfate ion may also occur in irradiated-fuel process feed solutions, e.g., from the use of sulfuric acid in dissolving stainless-steel matrix fuels, or by decomposition of sulfamic acid used in plutonium valence control. Lang and Nethaway at Mallinckrodt have recently reported[29] an extensive study of uranium distribution coefficients into a 30 per cent TBP–70 per cent hexane mixture for aqueous-phase concentrations as follows: uranium, 0 to 480 g/liter; nitric acid, 0 to 5.0*N*; and sulfate, 24 to 96 g/liter. A typical plot of the Lang and Nethaway data is given in Fig. II-5. Typically the uranium distribution ratio is decreased logarithmically about an order of magnitude as the sulfate concentration is increased from 0 to

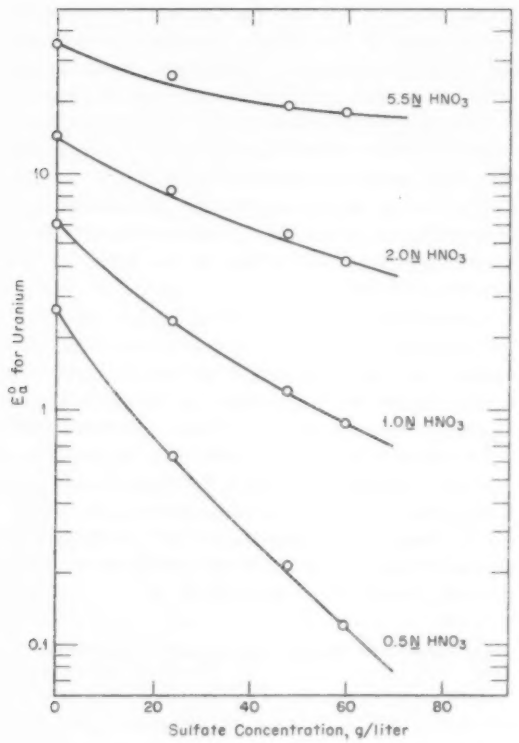

Fig. II-5 Effect of sulfate on the extraction of uranium by 30 per cent TBP.[29]

100 g/liter. This effect decreases with increasing acidity and uranium concentration.

Since the transfer of uranium between aqueous and organic phases involves a diffusion mechanism, the interpretation of the performance of solvent-extraction equipment is benefited by reliable data on diffusion coefficients. Ondrejcin at Savannah River has recently measured a series of integral diffusion coefficients in the aqueous phase (i.e., with a concentration gradient) for uranyl nitrate, nitric acid, and aluminum nitrate in concentration ranges of interest in fuel processing and has reported these along with data for viscosity, density, and surface tension of the solutions used.[30]

The separation of plutonium from uranium by solvent extraction generally requires that the plutonium be reduced to the trivalent state. Ferrous sulfamate is now used for this purpose, but the iron and sulfate compounds that are produced are undesirable in the process waste. A solution of a tetravalent uranium compound, which might be prepared from the uranium product stream, would provide a reductant that would not increase the salt content of the waste stream. Katz[31] has noted that available methods of reducing the uranium in uranyl nitrate solution to the tetravalent state are complicated and expensive and has recommended a sulfide process for this purpose. Precipitation of uranyl sulfide provides a low-temperature means of preparing uranium dioxide in a soluble form. Uranyl sulfide is precipitated by addition of 1.4*M* uranyl nitrate to about a 50 per cent excess of 2.5 per cent ammonium sulfide, followed by digestion for 90 min at 40°C to decompose uranyl sulfide to uranium dioxide and sulfur. After separation of solids from the supernatant, uranium dioxide is dissolved in 4*M* nitric acid at 60°C, and the sulfur is filtered off. A solution containing 83 g of uranium per liter, of which 71 per cent is in the tetravalent state, may thus be produced.

At Los Alamos studies are being made to develop a solvent-extraction method for the recovery of plutonium from various pyrometallurgical process streams.[32] In solvent extraction of plutonium from feed solutions having a 7*M* nitrate concentration with a mixture of a secondary amine (LA-1) and tetrachloroethylene (TCE), the plutonium distribution coefficient was greatly affected by acidity in the range 0.5*M* to 1.5*M* with higher coefficients being obtained at low acidity. Ferrous ion was effective in stripping plutonium at low acidity in the absence of nitrate.

Processing of fuel in the thorium-U^{233} breeding cycle is likely to involve some form of remote refabrication because of the rapid buildup of activity in the recovered products. Consequently, in considering the application of solvent extraction in such a cycle, a relatively simple operation effecting only moderate decontamination from neutron poisons may be useful. Experiments at Oak Ridge were aimed at the quantitative simultaneous recovery of uranium, thorium, and protactinium. By extraction of 1 volume of aluminum nitrate-salted, moderately acid feed with 2 volumes of 30 per cent TBP in diluent, followed by scrubbing with a solution of similar composition to the feed,

the uranium and thorium, with about half of the protactinium, were recovered with high rare-earth decontamination and with decontamination factors for ruthenium and zirconium-niobium of the order of 200 and 4, respectively.[25] The poor separation of zirconium is not thought to be a problem because of its low cross section.

The general use of solvent-extraction processes in nuclear fuel technology indicates the need for engineers in this field to have some understanding of the pertinent extraction-process principles. Makens and Bush[33] have described a simple mixer-settler apparatus and have suggested some experiments involving thorium-uranium separation with TBP appropriate for use in a nuclear engineering curriculum.

Alternate Solvent Systems

Although Purex type processes are based on the use of TBP diluted with a kerosenelike hydrocarbon mixture, numerous improvements and adaptations for special purposes have been made by the substitution of other diluents and other uranium complexing reagents. The instability of commercial hydrocarbon mixtures to the effects of irradiation and chemical (acid) attack have prompted many studies of the performance of specially purified hydrocarbon mixtures and of pure hydrocarbons from various sources. A recent contribution from Savannah River on this subject is a report by Chastagner[34] on the evaluation of a commercial dodecane that is designated "Adakane" and is prepared, presumably from fatty acid glycerides, by the Archer-Daniels-Midland Company. Analysis indicated the materials were about 90 per cent dodecane with a few per cent adjacent hydrocarbons, and the properties of the mixture were essentially those of dodecane. Chemical and radiolytic stability indices were almost the equivalent of pure dodecane and were markedly superior to those of typical petroleum-based diluents.

Korpak of the Polish Academy of Sciences has recently described[35] the alkyl sulfoxides (R_2SO) as a new class of compounds suitable for the extraction of uranium from acid solutions. The sulfoxides investigated were di-*n*-octyl, ethyl dodecyl, and dibenzyl. In equilibrium with a 0.1*M* nitric acid–4*M* sodium nitrate solution originally containing 1 g of uranium per liter, a solution of 0.04*M* dioctyl sulfoxide in carbon tetrachloride showed a uranium distribution coefficient of 0.5, compared to 0.4 for TBP under similar conditions. In other work from the Polish Academy of Sciences, Deptuła and Minc[36] have noted that tri-*n*-octylamine is about as effective in extracting uranium from sulfuric acid solutions as is dibutyl phosphoric acid and that, at sulfuric acid concentrations in the range 1*M* to 3*M*, combinations of the two extractants are considerably more effective than is either extractant alone at the same molar concentrations.

Laboratory studies at Oak Ridge of a trilaurylamine extraction process for final recovery and purification of plutonium were recently described.[37] In preparing for applications of this process, tests have been initiated on the performance of a pulse column on streams occurring in the process.[3] Flooding rates for extraction and stripping columns were comparable to those experienced in TBP processes. In alkaline washing of the stripped amine solvent, flooding rates were much lower.

Separation of Other Transuranic Elements

There is increasing interest in the separation of significant quantities of elements, other than plutonium, of greater atomic number than uranium. Some of this interest relates to the production of isotopic power sources, and some to efforts to obtain quantities of newer elements sufficient for the production of still higher elements by neutron irradiation.

Tetravalent neptunium is readily extracted by a variety of amine and phosphate derivatives from nitric acid solutions and in this valence state is much more extractable than are either the trivalent or the pentavalent forms. Weaver[38] has reported extensive studies at Oak Ridge on the extraction of neptunium at tracer levels from nitrate, sulfate, and chloride systems. Some of his data are summarized in Table II-2. ORNL is engaged in a program for the production of gram quantities of heavy-element isotopes up to Cf^{252} and smaller quantities of higher isotopes. Starting with target elements of Pu^{239} and aluminum, products will be separated and formed into new targets for reirradiation and subsequent separation. The High-Flux Isotope Reactor (HFIR), now under construction, and a new intense alpha-gamma processing facility (TRU), which is now being designed, will be the principal facilities used in this program.[39] One aspect of this program involves the separation

of the elements higher than plutonium from the rare-earth fission products.

In the rare-earth series, as in the transplutonium series of elements, elements within the group differ only slightly in chemical properties; in most chemical systems, each element in the transplutonium group behaves almost exactly like a corresponding element in the lanthanide series. Separations have previously been accomplished by ion-exchange resins in a small-scale batch fashion. For the proposed program the extremely high levels of radiation resulting from the concentrations and quantities of the elements of interest are likely to make the use of solid ion-exchange materials impractical.

Baybarz and others[40,41] at Oak Ridge have developed a solvent-extraction system which is capable of a very high degree of separation of lanthanides from the transplutonics and which shows significant separation among the transplutonics. The latter are extracted from a concentrated chloride system by a tertiary amine contained in an aromatic hydrocarbon diluent, as shown by the flow sheet in Fig. II-6. The feed solution is 11*M* lithium chloride containing a trace of hydrochloric acid, and the extractant is a mixture of tertiary hexyl and octyl amines at a 0.6*M* concentration in diethylbenzene. A single stage yields a separation factor of the order of 100; thus only a few stages should be needed.

Extraction is very strongly dependent on chloride concentration (to the 15th–20th power),

Table II-2 DISTRIBUTION COEFFICIENTS FOR NEPTUNIUM

(Tracer Neptunium in 1*M* Nitric Acid Solutions)

Extractant compound	Conc., *M* (in hydrocarbon diluent)	Distribution coefficient (E_a^o)
Primene JM-T	0.1	0.004
Triisooctyl amine	0.1	2.0
Tetraheptyl ammonium nitrate	0.01	220
Tributyl phosphate	1.0	0.7
Di-*sec*-butylphenyl phosphonate	1.0	0.8
Di-*n*-butylphenyl phosphonate	1.0	1.5
Diamylamyl phosphonate	1.0	60
Di-2-ethylhexyl phosphoric acid	0.01	600
Trioctyl phosphine oxide	0.01	45

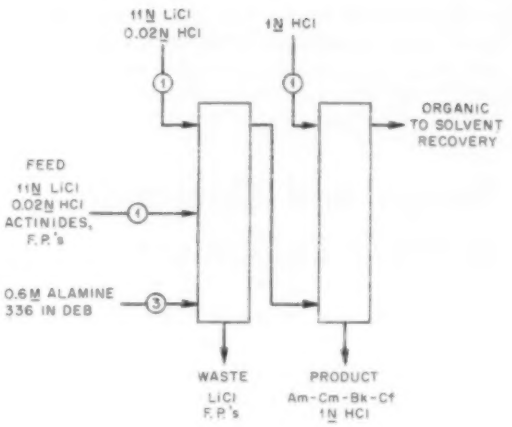

Fig. II-6 Actinide-lanthanide separation flow sheet.[40]

and only the lithium and calcium salts are sufficiently soluble to provide about a 10*M* chloride concentration. The lower viscosity of lithium chloride solutions favors its use, although mixtures with up to 2*N* aluminum chloride may also be used. The separation of lanthanides from actinides decreases as acidity increases; thus a nearly neutral solution is favored. An aromatic diluent is preferred because the use of a modifier such as tridecanol in an aliphatic diluent is necessary to prevent formation of a third phase. The amine reagent appears to be satisfactorily stable to irradiation levels up to about 25 watt-hr/liter.

For separation of the individual transplutonium elements, extraction with a solution of 2-ethylhexylphenyl phosphoric acid from chloride systems is being investigated.[21] Californium was readily separated from americium in 1.4*N* hydrochloric acid.

Process Instrumentation

Chester at ORNL reports[42] on the development of an apparatus for measuring interfacial viscosity. Such data might make possible the correlation of extraction-column system performance. Many investigators have found that interfacial phenomena can have a profound effect on the rate of mass transfer in solvent extraction. Such an instrument could also be useful in determining causes of extraction-process problems as well as in evaluating the beneficial effects of surface active agents added

to extraction systems. The report describes the first model of the apparatus, shown in Fig. II-7, and cites several measurements using distilled water and mixtures of distilled water and a commercial detergent.

Design and Operation of Plant Equipment

Weech et al. report[43] more fully on the extraction-column air pulser described previously.[37] The report includes a section on the mathematical representation of the system. Referring to Fig. II-8, valves V_1 and V_2 admit and release air to and from the air space above the liquid level in the leg. In practice, these valves are opened and closed by a speed-regulated cam arrangement. Air is supplied from a reservoir that serves to damp the pressure fluctuations. Pressure in the reservoir is regulated very closely by a proportional type pressure controller. There are only two controls on the system: (1) the speed control on the mechanism that opens and closes valves V_1 and V_2 and (2) the pressure controller that adjusts the air pressure supplied to V_1.

Assume that the column and the adjacent leg shown in Fig. II-8 are filled with liquid to a

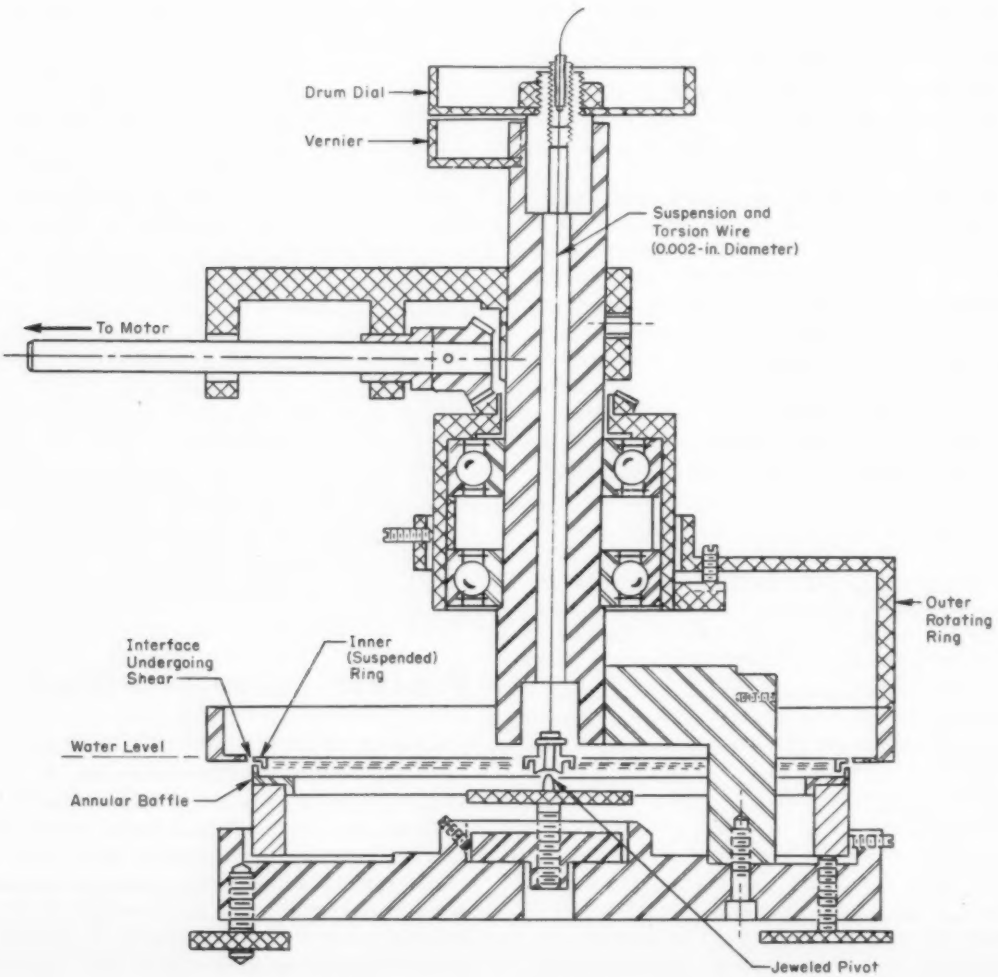

Fig. II-7 Interfacial viscosimeter (set up for air-water interface).[42]

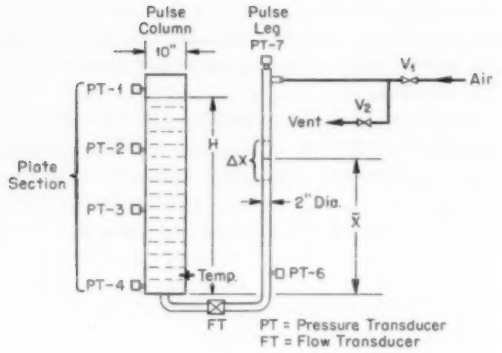

Fig. II-8 Experimental column schematic diagram.[43]

level above the plate section. Valve V_2 is open and V_1 is closed so that the liquid level equalizes between the column and leg. Air is supplied at constant pressure to valve V_1. Valve V_2 now closes and V_1 opens. This valve action admits air pressure into the chamber above the liquid level in the leg, and this pressure depresses the level in the leg, transferring some liquid from the leg into the column. Valve V_1 now closes and V_2 opens. This vents the air pressure from the chamber above the liquid level in the leg, and, since the level in the leg was depressed from its equilibrium position, there is a greater hydrostatic head in the column than in the leg; thus fluid flows from the column to the leg, and the leg liquid level rises. The interchange of fluid between the leg and the column results in a pulsing action of the column liquid. The magnitude of the column pulse is set largely by the air pressure applied through V_1, and the frequency is set by the time cycle at which valves V_1 and V_2 are opened and closed. Amplitude, however, for a given pressure setting, is not independent of frequency. In practice, for any given frequency-amplitude combination, the liquid level in the leg will stabilize at some mean position $\overline{X}$ (see Fig. II-8) and will move up and down the distance ΔX, as dictated by the pressure-frequency settings. From this an equation is developed for fluid mass and inertia:

$$F = \frac{\ddot{X}}{g}\left[\rho_L X + \rho_m H \left(\frac{A_L}{A_C}\right)\right]$$

For fluid friction:

$$\text{Leg friction force} = \frac{2f\,\rho_L\,(R+X)\,(\dot{X})^2}{gD}$$

$$\text{Plate friction force} = \frac{\rho_m N}{2gC^2}\left(\frac{A_L}{A_0}\right)^2(\dot{X})^2$$

These are combined into a final equation to represent the air pulser performance, where:

$$\left[\frac{\rho_m H}{g}\left(\frac{A_L}{A_C}\right) + \frac{\rho_L X}{g}\right]\ddot{X}$$

$$+\left[\rho_m\left(\frac{A_L}{A_0}\right)^2\frac{N}{2gC^2} + 2f\,\rho_L\frac{(R+X)}{gD}\right](\dot{X})^2$$

$$+\rho_m H - \rho_L X = -F(P,t)$$

The $\rho_m H$ term is the liquid head in the column that acts against the applied air pressure:

A_L = pulse leg area
A_C = column area
A_0 = plate free area
ρ_L = density of liquid in the leg
X = height of fluid in the leg
$\ddot{X} = d^2X/dt^2$
ρ_m = mean density of the fluid in the column
N = number of plates in the column
C = orifice coefficient
f = friction factor
R = equivalent length of line (leg)(bends, etc.)
D = line diameter (leg)
$\dot{X} = dX/dt$

$F(P,t)$ is the air pressure that is applied to the liquid in the leg in which the pressure is a function of the time and varies with the system geometry. This has not been expressed in explicit terms at this time.

Solution of this equation was accomplished using an analog computer. Results were used to design a column pulser for installation in the ICPP.

Corrosion

The method now used at ICPP for recovering uranium from zirconium-matrix fuels consists of dissolution of the fuel in a mixture of nitric and hydrofluoric acids, followed by solvent extraction to effect separation. The concentration of uranium in the solvent-extraction feed streams is limited by the very large amounts of dissolved zirconium from the fuel matrix. The presence of zirconium also governs the volume of liquid wastes which are generated and which must be stored permanently. Further,

since a large quantity of hydrofluoric acid is necessary to solubilize the zirconium, a large amount of aluminum nitrate is subsequently required to inhibit properly the corrosive attack of the solutions in the processing equipment. With these particular problems in mind, ICPP has been conducting an experimental program to reduce the zirconium content of dissolver solutions by precipitation methods. The first method consisted of the precipitation of barium fluozirconate by the prior addition of barium nitrate. Preliminary corrosion evaluations made on this system have been reported in previous Reviews.

An alternative method that is being explored for the precipitation of zirconium from dissolver solutions employs the addition of sodium formate. Several preliminary corrosion tests have been performed to determine what construction materials might be used for this process or, alternatively, to determine the compatibility of existing plant materials.[44] Tests were made at 60°C using unwelded coupons of stainless-steel type 316L, Carpenter-20, Monel, and Hastelloy F in each of two environments. The first environment was characteristic of dissolver solutions prior to the addition of a precipitation agent, and the second was characteristic of the slurry resulting from the addition of sodium formate. The reference dissolver solution for each of the two tests was 1.6*M* zirconium, 1.6*M* hydrogen ion, 8*M* fluoride ion, and 0.03*M* chromic acid. The chromic acid is needed in the flow sheet to retain the uranium in the hexavalent state and thereby reduce uranium losses to the precipitate. The results are shown in Table II-3. Of the four materials tested, it is evident that Monel is the only material that is not compatible with the environments.

The electrolytic dissolution of reactor fuels is being studied at Idaho and Savannah River. This method is attractive because it affords the possibility of processing a variety of fuels, including stainless-steel and zirconium-matrix fuels, in a common plant. The results of corrosion evaluations at both of these sites have been reported periodically in this Review. In the April 1962 issue of *Reactor Fuel Processing*, it was reported that Idaho had exposed electrically isolated stainless-steel type 304 coupons in a laboratory electrolytic dissolver during the dissolution of austenitic stainless-steel fuel under refluxing conditions. Although the test specimens were isolated electrically, considerable variation in corrosion was observed. Those specimens which were reasonably well shielded from stray currents suffered relatively low rates of attack. However, those which were in the current path exhibited localized attack on the anodic side of the specimen. These experiments were extended to niobium and titanium to determine whether they, too, were sensitive to stray current effects.[44] Both metals showed a slight increase in weight during exposure, and no localized effects were observed. It appears, therefore, that these metals would be satisfactory for those applications where stray currents are likely to be encountered.

Plastic specimens that have been considered as possible electrical insulating and supporting

Table II-3 CORROSION DURING THE PRECIPITATION OF ZIRCONIUM AND FLUORIDE WITH SODIUM FORMATE[44]

(Conditions: Temperature = 60°C; Dissolver Solution Composition = 1.6*M* Zr, 1.6*M* H^+, 8*M* F, 0.03*M* Chromic Acid, 3.7 g/liter U; Length of Test = 48 hr)

Construction material, unwelded	Corrosion in dissolver solution, mils/month			Corrosion in slurry* containing flocculating agent,† mils/month			Corrosion in slurry* without flocculating agent, mils/month		
	Liquid	Interface	Vapor	Liquid	Interface	Vapor	Liquid	Interface	Vapor
S.S. 316L	0.79	2.1	1.6	0.03	Nil	Nil	Nil	Nil	Nil
Monel	25‡	5.8	Nil	2.5	0.99	0.18	9.1	4.3	0.42
Hastelloy F	0.52	0.63	0.32	0.03	0.04	0.02	0.07	0.08	0.07
Carpenter-20	0.53	0.33	0.24	Nil	Nil	Nil	Nil	Nil	Nil

*Dissolver solution with 2 moles of sodium formate per mole of zirconium.

†Six cubic centimeters of 1 per cent Jaguar-Flocculation-Filter Aid (manufactured by Stein, Hall & Co., Inc., New York) per 50 cc of dissolver solution.

‡Pitted.

materials for use in an electrolytic dissolver were tested by irradiating them to 10^9 r in the dissolver product solution in the gamma facility at the Materials Testing Reactor (MTR) at Idaho.[44] The solution was 1*M* nitric acid and contained 75 g of dissolved stainless steel per liter as nitrates; the test temperature was 101°C. In the absence of irradiation, the following four materials were found to be satisfactory: Saran, Kynar, Kel-F, and Marlex-50. When subjected to irradiation in the dissolver solution, the first three plastics underwent cracking and crazing. Only the Marlex-50 appeared to resist the environment adequately enough to warrant further testing.

Corrosion in the heat exchanger of an experimental pilot-plant waste calcining unit at Idaho was recently measured.[44] The primary source of heat for this calciner is hot sodium-potassium alloy that derives its heat from a heat exchanger through an auxiliary oil-fired furnace. The heat-exchange surfaces are in the form of a bundle of tubes that are constructed from type 316 stainless steel. These tubes have been in operation for a total of 9100 hr. Of this exposure, 6360 hr were at temperatures in excess of 1000°F and the balance at 200 to 1000°F. Visual examination of the tube bundle suggested that the stainless steel had suffered only minor corrosion damage. All tubes were coated with a porous, rather tenacious, uniform scale. Numerous pits, which were estimated to be less than 5 mils in depth, were observed under the scale. Of the areas examined by micrometer measurements, the top and bottom 3.0-in.-OD headers and the 1.5-in. manifold tubes suffered the most severe metal losses. The over-all corrosion rates of these components, based on total exposure, were 2.0 and 2.8 mils/month, with values of 2.7 and 3.7 mils/month when calculated for exposure times at temperatures in excess of 1000°F. Comparison of these data with a prior evaluation made after 6100 hr of service indicates a lower over-all corrosion rate in the last 3000 hr of exposure as compared to the earlier period. As a result of this evaluation, it was concluded that the tube bundle is suitable for continued use.

Evidence that the Carpenter-20Cb dissolver at ICPP has been performing satisfactorily from a corrosion point of view has been obtained from a corrosion specimen that had been inserted in this unit for the last 1000 hr of operation. The unit is used for aqueous dejacketing and dissolution of stainless-steel-matrix fuels. The flow sheets used during this time were those which were applicable to the processing of fuel elements from the Submarine Intermediate Reactor (SIR) and the Organic-Moderated Reactor Experiment (OMRE). The dissolution medium for these flow sheets is boiling sulfuric acid. The plant test specimen consisted of an as-welded 2-in.-high by 2-in.-diameter cylinder. The general corrosion that was observed was 2.3 mils/month with a small amount of interdendritic attack at weld areas. The amount of corrosive attack was about as expected and is considered reasonable.[44]

Brookhaven National Laboratory (BNL), in cooperation with the Savannah River Operations Office, is conducting a program to determine the best methods to be used for the chemical processing of various power-reactor fuels in existing facilities, with minimum modification, at Savannah River.[45] Primary efforts have been devoted to processing of stainless-steel-clad uranium dioxide fuels and, in particular, to the Sulfex process. An extensive investigation of corrosion of various construction materials by the reagents that are to be used is nearly complete, and results indicate that Nionel is the most satisfactory material. Observed corrosion rates were 25 mils/year in 4*M* sulfuric acid and 2 mils/year in sulfuric acid of the same molarity containing dissolved stainless steel. This confirms the earlier conclusions reached by ORNL and Hanford that Nionel is a satisfactory material for this environment. It further confirms the effect observed at Oak Ridge that the accumulation of dissolved stainless steel in the acid reduces corrosion rates. Hanford data have indicated that rates of attack increase with increasing dissolved stainless-steel content.[46]

In addition, an investigation is under way at Brookhaven[45] of the possibility of dissolving stainless-steel fuel in a stainless-steel vessel. Small amounts of nitric acid in sulfuric acid will passivate stainless steel, thus preventing it from dissolving. Passivation of stainless-steel fuel can be overcome by contacting the stainless steel with a mild-steel wire. Therefore it is thought possible to initiate selectively the dissolution of a stainless-steel fuel element while maintaining the vessel in a state of passivation. However, the hydrogen evolved from the dissolution rapidly reduces the nitric acid to nitric oxide, and the vessel is then subse-

quently attacked. An attempt is being made to overcome this by using a downdraft condenser and introducing oxygen into the cold leg to oxidize the nitric oxide to nitrogen dioxide. The nitrogen dioxide can be reabsorbed in the condensing vapors, which are then returned to the dissolver. The nitric acid concentration can thus be maintained. Results have confirmed the feasibility of this technique, and a detailed study of the effects of the variables affecting condenser design is in progress.

ORNL has continued to study the possibility of developing a zirconium-dissolution process that would be compatible with titanium equipment.[25] Such a process would make it possible for the same titanium equipment to be used for the dissolution of both stainless-steel- and zirconium-matrix fuels. In a current report[47] the results of a series of dissolution and corrosion rate tests are reported for an environment that consists of chromium-inhibited nitric acid–fluoboric acid solutions, with and without the addition of hydrofluoric acid. Hexavalent chromium ion probably serves to produce a protective oxide coat on titanium, thus preventing its attack by fluoride ion. Fluoboric acid apparently also forms a protective white compound that coats the titanium surface. This coat is not sufficiently protective unless the reagent contains fluoride ion other than that supplied by hydrolysis of fluoboric acid. This suggests that the coat is actually a fluoborate rather than a borate compound. The chromium inhibitor was present in both the hexavalent and trivalent states, since the former is reduced to the latter

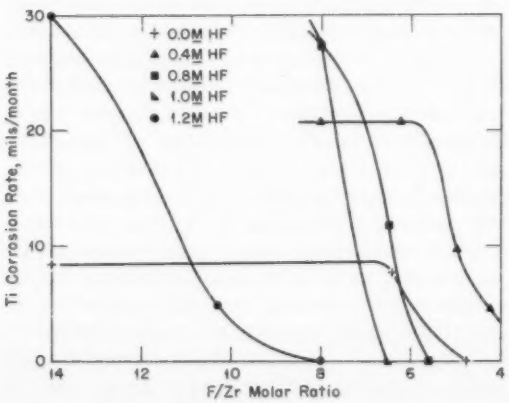

Fig. II-9 Titanium corrosion rates in refluxing $3M$ HNO_3–$0.4M$ HBF_4–$0.4M$ to $1M$ Cr-HF-Zr.[47]

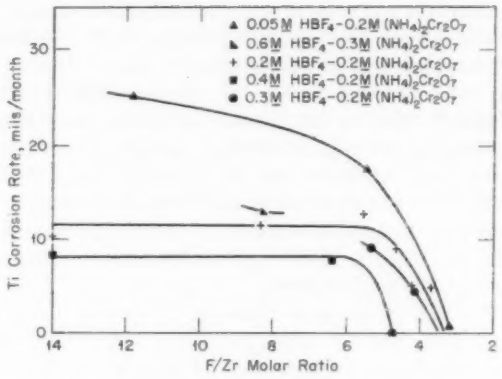

Fig. II-10 Corrosion rate of titanium in refluxing $3M$ HNO_3–HBF_4–$(NH_4)_2Cr_2O_7$–Zr solutions.[47]

by dissolving zirconium alloys. In view of this continuous reduction process, it was necessary to maintain more than the required stoichiometric amount of hexavalent chromium to keep titanium corrosion rates low. Increasing the fluoboric acid content to $0.4M$ had the surprising effect of further decreasing titanium corrosion rates. Increasing this concentration above $0.4M$ increased the corrosion rate. When $0.4M$ hydrofluoric acid was added to refluxing $3M$ nitric acid–$0.4M$ fluoboric acid–chromium in the presence of zirconium, the titanium corrosion rate increased and remained high until the fluorine-to-zirconium ratio dropped to 5. However, at higher hydrofluoric acid concentrations (to a molarity of 0.8 to 1.2), corrosion rates were initially higher, but they dropped rapidly at larger fluorine-to-zirconium ratios. The effect of hydrofluoric acid concentrations is shown in Fig. II-9 and of fluoboric acid concentrations in Fig. II-10.

A number of graphite- and uranium carbide-containing fuels have been proposed for power-reactor use. One such fuel is the core alloy from the TRIGA reactor. In an earlier Review, corrosion tests were reported for stainless-steel type 309SCb in a mixture of 90 per cent fuming nitric acid–10 per cent fuming sulfuric acid at relatively low temperatures. The purpose of treating the TRIGA core alloy fuel in this solution was to disintegrate it prior to dissolution. In a current report,[25] it was proposed to disintegrate such fuel in $20M$ nitric acid (90 wt.%). Specimens of titanium-45A, a candidate construction material, were exposed in the welded condition to the solution, interface,

and vapor phase of a boiling solution containing 20*M* nitric acid, 50 g of uranium per liter, and 20 g of solid graphite per liter. The maximum observed corrosion rate during the initial 24-hr test period was 0.2 mil/month, and this rate gradually decreased by a factor of 20 to 3 over the course of six additional exposure periods. Titanium appears, therefore, to be a very satisfactory construction material for a dissolver in this system provided that fluoride is not added in subsequent processing steps. Because of the possibility of such fluoride addition in certain proposed flow sheets, other materials will be evaluated in this system.[25]

At ORNL plans are progressing for the isolation of transuranium elements. Processes presently envisioned make use of concentrated chloride solutions covering a wide range of acidities; in some steps, nitrate will also be present. In all solutions containing an appreciable concentration of the transuranium elements, peroxide is expected to be present as a product of the radiolysis of water. It is expected that the most difficult environment to contain will be hydrochloric acid in a container that contains transuranium elements. Tests lasting from 24 to 840 hr have been run on 10 materials in a number of solutions that have been proposed for various steps in the flow sheet.[25] Of the materials tested in 6*M* hydrochloric acid in the presence of 0.0015*M* peroxide at 105°C, zirconium and Zircaloy-2 appeared to be the most generally satisfactory construction materials (corrosion was less than 1 mil/month). In acid waste solutions containing nitric acid, hydrochloric acid, aluminum nitrate, and lithium chloride, stainless steels 304L and 309SCb had rates of attack in excess of 500 mils/month. This compared with values of less than 4 mils/month for Hastelloy C, Haynes-21 and -25, and zirconium. Corrosion was acceptable for all materials when the above wastes were neutralized.[25]

The effect that cold work on austenitic stainless steels has on the corrosion of these alloys in boiling 65 per cent nitric acid is being examined at Hanford.[48,49] Prior to testing, the samples were annealed at 1975°F for 1 hr and quenched rapidly in water. The samples were subsequently cold worked to an extent of a 10 to 60 per cent reduction in cross-sectional area. These samples and a control were exposed in boiling 65 per cent nitric acid. In a total of ten 24-hr periods of exposure for each sample, no significant effects were observed on the corrosion rate between the various samples.

Difficulties have often been experienced at the chemical processing sites in the handling of waste solutions at near boiling temperatures as, for example, in volume reduction by evaporation. Both Hanford and Idaho have found that, for specific applications involving concentrators, titanium appears to have considerably greater resistance to the accumulation of dissolved corrosion-product chromium than do the higher austenitic stainless steels such as types 309 and 310. Hanford has been testing titanium under a variety of waste processing conditions in an effort to determine what limitations it might have.[48–52] Specimens are exposed to simulated Purex 1WW environments containing concentrations of fluoride six times higher than those expected in routine operations. In addition, a series of corrosion tests was made in which the titanium specimens simulated the conditions of heat-transfer surfaces under refluxing conditions up to 160°C, which was above the atmospheric boiling point of the liquid environment. In none of these tests has a corrosion rate in excess of 1 mil/month been observed. Critical evaluations for evidence of crevice attack at gasket-sample contact points have shown no evidence of such corrosion. It appears that titanium has very high resistance to nearly all conditions expected in the processing and handling of unneutralized waste materials.

Huey tests* have been performed on 30 type 304L stainless-steel tubes taken from a uranyl nitrate hexahydrate concentrator that failed during operation. Results of the tests on these tubes were compared against a standard sensitized type 304L stainless-steel specimen that corroded at a rate of 1.4 mils/month. A total of four samples corroded at rates in excess of 5 mils/month, and four of these samples corroded at rates in excess of 10 mils/month. These results indicate that the stainless steels used for the construction of the uranyl nitrate hexahydrate concentrator were probably substandard as evaluated by the Huey test.[48]

*A quality-control test (designated ASTM A262-52T) for determining primarily the susceptibility of corrosion-resistant steels to subsurface attack. The test consists of exposure to boiling 65 per cent nitric acid in five 48-hr periods (fresh acid for each period) under prescribed conditions.

References

1. B. C. Finney, in Unit Operations Section Monthly Progress Report, September 1961, USAEC Report ORNL-TM-112, pp. 27–34, Oak Ridge National Laboratory, Apr. 5, 1962.
2. *Reactor Fuel Processing*, 5(1): 8 (January 1962).
3. B. C. Finney, in Unit Operations Section Monthly Progress Report, October 1961, USAEC Report ORNL-TM-121, pp. 18–21, Oak Ridge National Laboratory, Apr. 5, 1962.
4. R. A. Ewing et al., Sulfex-Thorex and Darex-Thorex Dissolution of High Burnup Consolidated Edison Reactor Fuel, USAEC Report BMI-1560, Battelle Memorial Institute, Dec. 21, 1961.
5. T. A. Gens, The Chemistry of Niobium in Processing of Nuclear Fuels, USAEC Report ORNL-3241, Oak Ridge National Laboratory, Feb. 5, 1962.
6. *Reactor Fuel Processing*, 4(1): 16 (January 1961).
7. W. W. Schulz et al., Nitric Acid Dissolution of Uranium-Molybdenum Alloy Reactor Fuels, *Ind. Eng. Chem.*, 1(2): 156–160 (April 1962).
8. S. Goldsmith et al., Hanford Atomic Products Operation, Jan. 20, 1961. (Unpublished)
9. S. Goldsmith et al., Hanford Atomic Products Operation, Mar. 1, 1962. (Unpublished)
10. *Reactor Fuel Processing*, 4(2): 13 (April 1961).
11. E. M. Vander Wall et al., Salt Phase Chlorination of Reactor Fuels. III. Catalyzed Dissolution of Uranium Dioxide in Lead Chloride–Chlorine Systems, USAEC Report IDO-14578, Phillips Petroleum Co., Feb. 5, 1962.
12. T. A. Gens, Zircex and Modified Zirflex Processes for Dissolution of 8% U–91% Zr–1% H TRIGA Reactor Fuel, USAEC Report ORNL-3065, Oak Ridge National Laboratory, Nov. 30, 1961.
13. *Reactor Fuel Processing*, 4(4): 9 (October 1961).
14. M. E. Whatley et al., Chemical Technology Division, Unit Operations Section, Monthly Progress Report, May 1961, USAEC Report ORNL-TM-33, Oak Ridge National Laboratory, Dec. 26, 1961.
15. M. E. Whatley et al., Chemical Technology Division, Unit Operations Section, Monthly Progress Report, August 1961, USAEC Report ORNL-TM-65, Oak Ridge National Laboratory, Mar. 1, 1962.
16. J. A. McBride, Idaho Chemical Processing Plant, February 1962. (Unpublished)
17. M. R. Bomar, Electrolytic Oxidation of Zirconium in Nitrate Solutions, USAEC Report IDO-14571, Phillips Petroleum Co., Dec. 29, 1961.
18. J. H. Owen (Comp.), Processing of Power Reactor Fuels, 15th Quarterly Progress Report, April 1–July 1, 1961, USAEC Report DP-626, Savannah River Laboratory, September 1961.
19. J. R. Aylward et al., Electrolytic Dissolution of Nuclear Fuels. Part I. Zirconium in HCl-Methanol, USAEC Report IDO-14573, Phillips Petroleum Co., Dec. 29, 1961.
20. J. R. Aylward and E. M. Whitener, Dissolution of Zirconium in HCl-Methanol, *J. Electrochem. Soc.*, 109(2): 87–91 (1962).
21. F. L. Culler, Jr., Chemical Technology Division Monthly Report for February 1962, USAEC Report ORNL-TM-151, Oak Ridge National Laboratory, Mar. 2, 1962.
22. *Reactor Fuel Processing*, 4(4): 20 (October 1961).
23. J. R. Aylward and E. M. Whitener, Electrolytic Dissolution of Nuclear Fuels. II. Nichrome in Nitrate Solutions, USAEC Report IDO-14575, Phillips Petroleum Co., Dec. 29, 1961.
24. L. M. Ferris et al., Processes for Recovery of Uranium and Thorium from Graphite-Base Fuel Elements. Part II, USAEC Report ORNL-3186, Oak Ridge National Laboratory, Nov. 30, 1961.
25. R. E. Blanco, Quarterly Progress Report for Chemical Development Section B, July–September 1961, USAEC Report ORNL-TM-81, Oak Ridge National Laboratory, Jan. 26, 1962.
26. M. E. Whatley et al., Chemical Technology Division, Unit Operations Section, Monthly Progress Report, July 1961, USAEC Report ORNL-TM-35, Oak Ridge National Laboratory, Jan. 30, 1962.
27. K. S. Warren et al., Dissolution of BeO- and Al_2O_3-Base Reactor Fuel Elements. Part I, USAEC Report ORNL-3220 (Pt. I), Oak Ridge National Laboratory, Feb. 14, 1962.
28. *Reactor Fuel Processing*, 5(1): 12 (January 1962).
29. G. P. Lang and M. O. Nethaway, The Effect of Sulfate on the Extraction of Uranium by Diluted Tributyl Phosphate, USAEC Report MCW-1456, Mallinckrodt Chemical Works, Uranium Div., Dec. 22, 1961.
30. R. S. Ondrejcin, Physical Properties of Uranium Process Solutions, USAEC Report DP-653, Savannah River Laboratory, October 1961.
31. H. Katz, Some Methods of Preparing Tetravalent Uranium Solutions, USAEC Report BNL-691, Brookhaven National Laboratory, September 1961.
32. Los Alamos Scientific Laboratory, Quarterly Status Report on LAMPRE Program for Period Ending August 20, 1961, USAEC Report LAMS-2620, September 1961.
33. R. F. Makens and D. E. Bush, Solvent Extraction Experiments in Nuclear Fuels Processing, *Nuclear Sci. and Eng.*, 21: 71–78 (January 1962).
34. P. J. P. Chastagner, Evaluation of Adakane 12 for Purex Use, USAEC Report DP-601, Savannah River Laboratory, October 1961.
35. W. Korpak, Alkyl Sulphoxides as Solvents for the Extraction of Mineral Acids and Uranyl Nitrate, Polish Report PAN-191/IV, November 1960.
36. C. Deptuła and S. Minc, The Extraction of Organic Compounds by Mixed Extractants. I. Studies on the System: Uranium and Chromium–Sulfuric Acid–Tri-*n*-octylamine–Alkylphosphoric Acids–

Diluent, Polish Report PAN-209/IV, December 1960.
37. *Reactor Fuel Processing*, 5(2): (April 1962).
38. B. Weaver, Extraction of Neptunium from Acidic Solutions by Organic Nitrogen and Phosphorus Compounds, USAEC Report ORNL-3194, Oak Ridge National Laboratory, Oct. 19, 1961.
39. Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report, for Period Ending May 31, 1961, USAEC Report ORNL-3153, Sept. 21, 1961.
40. R. D. Baybarz and B. Weaver, Separation of Transplutoniums from Lanthanides by Tertiary Amine Extraction, USAEC Report ORNL-3185, Oak Ridge National Laboratory, Dec. 20, 1961.
41. R. D. Baybarz and H. B. Kinser, Separation of Transplutoniums from Lanthanides by Tertiary Amine Extraction. II. Contaminations, USAEC Report ORNL-3244, Oak Ridge National Laboratory, Mar. 7, 1962.
42. M. E. Whatley et al., Chemical Technology Division, Unit Operations Section, Monthly Progress Report, June 1961, USAEC Report ORNL-TM-34, Oak Ridge National Laboratory, Jan. 23, 1962.
43. M. E. Weech et al., Interim Report on the Development of an Air Pulser for Pulse Column Application, USAEC Report IDO-14559, Phillips Petroleum Co., Sept. 22, 1961.
44. J. R. Bower, Jr. (Ed.), Chemical Processing Technology Quarterly Progress Report, April–June 1961, USAEC Report IDO-14567, Phillips Petroleum Co., Nov. 10, 1961.
45. J. H. Reynolds (Ed.), Nuclear Engineering Department Progress Report, May 1–August 31, 1961, USAEC Report BNL-696, Brookhaven National Laboratory.
46. R. F. Maness, Power Reactor Fuels Reprocessing Progress Report on Corrosion Studies, USAEC Report HW-61662, Hanford Atomic Products Operation, Aug. 26, 1959.
47. T. A. Gens, Dissolution of Zirconium Reactor Fuels in Titanium Equipment, USAEC Report ORNL-TM-22, Oak Ridge National Laboratory, Oct. 11, 1961.
48. W. H. Reas, Chemical Research and Development Operation Monthly Report, September 1961, USAEC Report HW-71222C, Hanford Atomic Products Operation, Oct. 15, 1961. (Classified)
49. W. H. Reas, Chemical Research and Development Operation Monthly Report, October 1961, USAEC Report HW-71535C, Hanford Atomic Products Operation, Nov. 15, 1961. (Classified)
50. W. H. Reas, Chemical Research and Development Operation Monthly Report, November 1961, USAEC Report HW-71921C, Hanford Atomic Products Operation, Dec. 15, 1961. (Classified)
51. W. H. Reas, Chemical Research and Development Operation Monthly Report, December 1961, USAEC Report HW-72142C, Hanford Atomic Products Operation, Jan. 15, 1962. (Classified)
52. W. H. Reas, Chemical Research and Development Operation Monthly Report, February 1962, USAEC Report HW-72902C, Hanford Atomic Products Operation, Mar. 15, 1962. (Classified)

Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

The volatilities of uranium and plutonium hexafluorides have been proposed as a basis for processing various types of irradiated nuclear reactor fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase–gas phase halogenation processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in some of these dry halogenation processes to enhance reactor control.

Nitrofluor Process

Laboratory-scale work has continued at Brookhaven National Laboratory (BNL) on the nonaqueous nitrogen dioxide–hydrogen fluoride system for processing reactor fuel elements. A solution containing 25 mole % nitrogen dioxide is capable of dissolving a variety of fuel-element materials at satisfactory rates over a temperature range of 100 to 200°C. The dissolution reactions convert the fuel materials to complex fluorides which contain oxides of nitrogen and which have a low solubility in the solvent. In the case of zirconium alloy fuels, the zirconium appears as an insoluble complex salt after dissolution, whereas the uranium remains in solution. After separation of the uranium solution and evaporation of solvent, the uranium in the residue is converted to uranium hexafluoride by repeated contacts with bromine trifluoride.

A major problem associated with the Nitrofluor process continues to be demonstration of complete uranium recovery during fluorination. Several tests have been performed[1] to ascertain the factors that affect the conversion of the uranium residue ($NOUF_6$) to uranium hexafluoride with bromine trifluoride. A significant finding is that the addition of 5 wt.% bromine pentafluoride to bromine trifluoride gave good conversion (99.9 per cent) to uranium hexafluoride.

Short-term corrosion tests on Monel and aluminum oxide have been performed to evaluate these materials for use in the Nitrofluor process.[1] Aluminum oxide materials were unsatisfactory in 20 to 25 mole % nitrogen dioxide solvent solutions at 150°C. The corrosion of Monel specimens in similar nitrogen dioxide–hydrogen fluoride mixtures containing small quantities of added water was investigated in 18-hr tests at 20°C. Liquid-phase corrosion for solutions containing no more than 4.1 per cent water was 0.8 mil/month or less. Rates of 5.7 and 160 mils/month were observed in the liquid phase with 5.5 and 7.6 wt.% water, respectively.

Monel specimens were exposed to the 20 to 25 mole % solvent solution in both liquid and vapor phases for 5.7 days at an average temperature of 108°C. Although only slight corrosion was observed in the liquid phase, corrosion was severe in the vapor phase. Serious Monel corrosion has occurred during the evaporation-condensation step of the Nitrofluor process, especially in the region of condensing vapor. The corrosion of Monel during distillation of dissolver solutions was investigated[1] using a 20 mole % nitrogen dioxide–80 mole % hydrogen fluoride solution. Monel coupons in the condenser were badly etched and deeply pitted, whereas coupons in the stillpot showed only slight corrosion.

Fused-Salt Volatility Process

A fused-salt fluoride-volatility process is being developed at ORNL as a nonaqueous tech-

nique for processing zirconium-clad highly enriched uranium fuel elements or homogeneous molten-fluoride-salt fuels. In the case of the heterogeneous fuel, the zirconium and uranium are converted to their respective tetrafluorides in $NaF-ZrF_4$ or $NaF-LiF-ZrF_4$ melts, with hydrogen fluoride used as the oxidant. The dissolved uranium tetrafluoride is further oxidized, in a different vessel, to volatile uranium hexafluoride by contact with elemental fluorine. The uranium hexafluoride product is purified by an absorption-desorption cycle on sodium fluoride pellets and is collected in cold traps. For the homogeneous fuels the hydrofluorination step is not required.[2]

The nature and extent of corrosion in this process has previously been reported[3,4] and reviewed[5,6] for early versions of the hydrofluorination and fluorination vessels. A report recently issued[2] presents a detailed analysis of nondestructive tests conducted on the current version of the hydrofluorinator and fluorinator vessels of the fused-salt volatility-process pilot plant after an initial series of 14 experimental runs with the zirconium-base fuel. A general description of the pilot plant, including the results of the runs, and preliminary corrosion results have been reported[7] and reviewed[8] previously.

The present report[2] discusses the evaluation of vessel corrosion by visual inspection; also discussed are chemical analyses of corrosion product layers and deposits, studies of nickel, molybdenum, chromium, and iron entrainment in the off-gas from the system, gamma radiography and ultrasonic thickness measurements of the vessel walls, and some metallographic studies of corrosion specimens. In addition, wax replications were made of the interior walls of the hydrofluorinator, to check the radiographic results. Duplicate impressions showed that the maximum pitting depth in the vapor-phase region of the hydrofluorinator was 8 mils.

In the over-all evaluation, the modes, mechanisms, and rates of corrosive attack observed seem to agree well with previous experimental work. Significant bulk metal losses and moderate pitting attack were noted in both vessels. Maximum attack in the INOR-8 hydrofluorinator, which operated at temperatures from 500 to 650°C, occurred in the middle of the vapor region at a calculated corrosion rate of 20 mils/month, based on 765 hr of molten-fluoride-salt residence time, or at a calculated corrosion rate of 0.06 mil/hr, based on 338.5 hr of hydrogen fluoride exposure time. The L-nickel fluorinator, which operated at about 500°C, sustained maximum bulk metal losses in the lower vapor region at calculated rates of 28 mils/month based on 694 hr of salt residence time, or 0.9 mil/hr based on 30.9 hr of fluorine exposure time.

Calculations based on losses in wall thickness indicate that both vessels should be capable of handling approximately 100 additional dissolution runs about seven times as long as the exposure to date. These calculations take into account pitting corrosion in the hydrofluorinator but ignore effects resulting from intergranular or other forms of selective attack which may be present in both vessels.

Atomization of molten fluorides by spraying is being investigated at ORNL in connection with processing of fused salts.[9] Two possible applications are being considered. In the first application the freezing of the salt droplets provides feed of high surface-to-volume ratio for more rapid dissolution of salt in a liquid hydrogen fluoride solution used in the recovery of the molten salt from the core of the proposed molten-salt breeder reactor. The homogeneous fuel of this reactor contains Li^7F and BeF_2, which are sufficiently valuable to require recovery by separation from fission products. The presently proposed salt-recovery process uses as feed the salt residue after volatility recovery of the uranium and employs dissolution of the salt in liquid hydrogen fluoride, followed by a solids-separation step to remove insoluble fission-product fluorides. The purified salt product is obtained by evaporation of the liquid. A flow sheet is shown in Fig. III-1. This process has been reported[7,10] and reviewed[11] earlier.

A second possible application is the dropwise fluorination of uranium-bearing molten salt. A preliminary consideration of such a scheme at ANL was previously reported[12] and reviewed.[11] This earlier experimental work employed a single-phase spray nozzle and showed the technical feasibility of the general method; however, practical difficulties that were cited might prevent the attainment of an economic process. The present ORNL work[9] emphasizes development of a two-phase spray nozzle in which pressurized gas is used to atomize the liquid. This type of nozzle is considered to have advantages over the single-phase type.

Preliminary tests of the ORNL nozzle showed that sprayed salt, when collected in water, was mostly irregular particles smaller than 5 μ in diameter and, when collected dry, was mostly spheres 25 to 100 μ in diameter. A photograph of the nozzle is shown in Fig. III-2. Developmental work is continuing.[9]

Dry Halogenation Processes

Engineering studies on a process for recovering highly enriched uranium from zirconium-base nuclear fuels are being made at ANL.[13,14] The process scheme is based on the use of fluidization and volatility techniques to recover the uranium as uranium hexafluoride. The fuel material is immersed in a fluid bed of inert solids (aluminum oxide) and contacted with hydrogen chloride gas at 350 to 400°C to effect the separation of uranium from zirconium by volatilization of zirconium tetrachloride. Uranium, which remains in the bed as uranium trichloride, is recovered as uranium hexafluoride by fluorination at 350°C. Fixed beds of alumina are employed to retain uranium and other particulate matter entrained in the zirconium tetrachloride off-gas stream. Results of studies made with both upflow and downflow

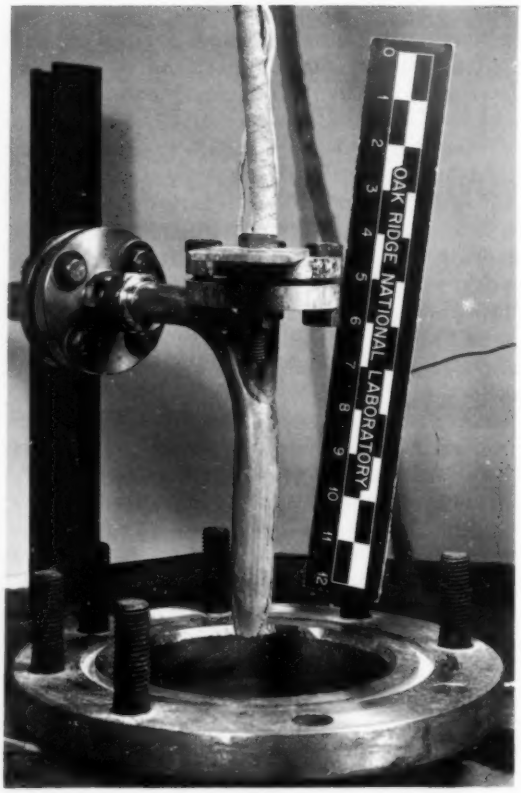

Fig. III-2 Two-phase atomizing nozzle for spraying molten salt.[9]

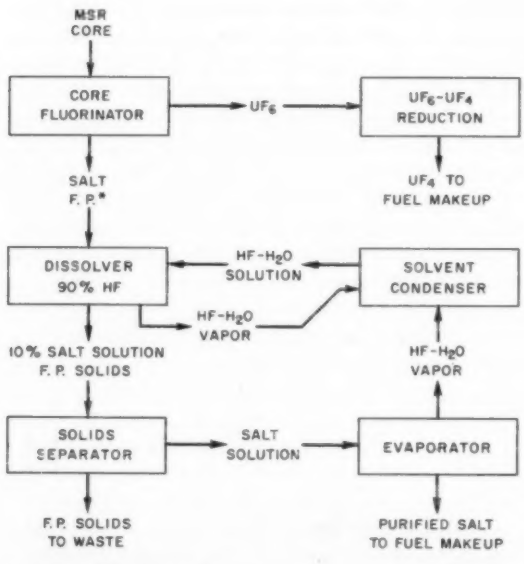

Fig. III-1 Proposed flow sheet for Molten-Salt Reactor (MSR) core fuel processing.[9]

filters in series show a uranium loss of only 0.1 per cent during hydrochlorination. The primary reaction vessel in these tests was a $1\frac{1}{2}$-in.-diameter nickel fluid-bed reactor (Fig. III-3). The upflow filter bed was a 3-in.-diameter section contiguous with the primary reaction section. The downflow bed ($1\frac{1}{2}$ in. in diameter) was contained in a separate unit. In an initial test, 270 g of alloy containing 4.8 wt.% uranium (charged as chips $\frac{1}{4}$ in. thick) was completely reacted in 6 hr using 50 mole % hydrogen chloride in nitrogen at 350°C. Fluorination for a period of 7 hr at 350°C effected the removal of 96 per cent of the uranium.

The processing of low-uranium-content zirconium alloy fuel by hydrochlorination will produce large quantities of waste zirconium tetrachloride. For irradiated fuel this product will be radioactive and, therefore, should be converted to a stable solid that can be stored

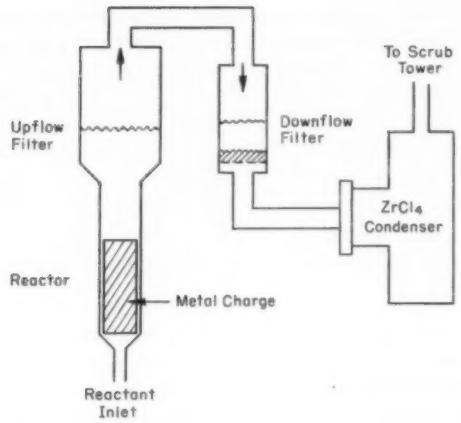

Fig. III-3 Fluid-bed uranium-zirconium alloy processing system.[14]

without difficulty. Conversion of zirconium tetrachloride to zirconium dioxide by pyrohydrolysis with steam occurs readily, and preliminary experiments have been carried out at ANL[14] to demonstrate this reaction in a fluid-bed system. Several successful tests have been made using a process gas stream containing 16 mole % zirconium tetrachloride in nitrogen. These tests were conducted in a 6-in.-diameter fluid-bed reactor using a 2-ft-deep bed of zirconium dioxide at a temperature of 400°C. Steam was supplied by the vaporization of an atomized water spray fed through a nozzle in the reactor wall. There are two possible modes of product distribution: (1) conversion may occur preferentially on the surface of the bed particles, which results in an adherent coating, or (2) a gas-phase reaction may occur which leads to the formation of fine particles. Preliminary results indicate that both modes of solid production occur.

Workers at BNL[1] have employed a fluidized-bed condenser to effect removal of zirconium tetrachloride from the off-gas stream. Zirconium tetrachloride is condensed on the surface of 60-mesh alumina particles maintained in a fluidized state. On completion of hydrochlorination, a steam–inert gas mixture is admitted to the condenser to convert the condensate to zirconium dioxide.

Direct Fluorination Processes

A direct fluorination volatility process is being developed at ANL to recover uranium and plutonium from spent uranium oxide, Zircaloy-clad or stainless-steel-clad, fuel elements. The proposed process for recovery of uranium and plutonium from the spent fuel involves decladding by an appropriate reaction in a fluidized bed. Plutonium and uranium hexafluorides, which result from the reaction of the declad oxide fuel with fluorine, may be separated from volatile fission products by distillation and separated from one another by thermal decomposition of plutonium hexafluoride.

Fluorination of Uranium Dioxide Pellets. The direct fluorination of dense uranium dioxide pellets is being examined in a 3-in.-diameter air-cooled reactor. The dense pelleted fuel material has been shown to be capable of fluorination at a practical rate in a fluidized bed of inert aluminum oxide particles. The bed of particles, which covers and fills the void spaces of the packed bed of oxide pellets, achieves many of the advantages of fluidization, particularly with respect to heat transfer and temperature control.

In the fluorination of uranium dioxide pellet fuel, the presence of oxygen has a pronounced effect on the reaction due to the formation of fine particles of U_3O_8. To obtain information for optimizing the conditions for the reaction of uranium dioxide pellets with fluorine-oxygen mixtures, several experiments were carried out to measure the rate of oxidation of oxide pellets in a 32 per cent oxygen–68 per cent nitrogen mixture.[14] It was observed that the rate of oxidation was moderate at 400°C and very rapid above 500°C. Oxidation of a 3-in.-deep pellet bed (2.2 kg of uranium dioxide) was virtually complete in 1.3 hr at 600°C and in 4.0 hr at 500°C. The heat transfer was not considered good in those tests in which relatively high oxidation rates were employed. The oxide residue consisted mostly of particles finer than 325 mesh with a mean diameter of approximately 20 μ. These results indicated that the concentration of oxygen should be limited in the reactor to avoid excessive fines production during fluorination of deep beds of uranium dioxide pellets. The oxide powder residues appeared very reactive in subsequent fluorinations. However, the heat transfer was not satisfactory.

To approximate more closely the expected processing conditions, fluorination tests using larger batches of pellets (18-in.-deep beds)

have been carried out.[14] These tests were conducted at 450°C with a fluidizing gas velocity of 0.5 ft/sec. It was observed that, when maximum off-gas recycle was employed as a measure to increase fluorine utilization, severe caking of the bed resulted. Although this recycle system has worked successfully in previous tests with 6-in.-deep beds, it appeared that high, uncontrolled oxygen concentrations in the recycle stream from the deep oxide bed contributed directly to caking of the bed. Fluorination of an 18-in.-deep pellet bed was carried to completion without gas recycle using nitrogen as a fluorine diluent. Absence of recycle prevents caking but results in a lower fluorine utilization efficiency.

Fluorination of Plutonium Dioxide. Since the inert fluid-bed solids will be discarded as wastes after fluorination of the oxide pellets is completed, it is important that very little uranium or plutonium be retained with the solids. A series of laboratory tests[15] has been made to determine the properties of the solids that may affect uranium or plutonium retention during fluorination. Satisfactory removal of uranium upon fluorination of mixed uranium-plutonium oxides was achieved at various temperatures (350 to 500°C) when zirconium tetrafluoride and calcium fluoride were used as bed materials. However, satisfactory removal of plutonium was not obtained using the same bed materials. Fluorination of the mixed oxides with Alundum (crystalline aluminum oxide) as bed material resulted in low plutonium concentrations (0.035 per cent residual plutonium in Alundum) after a 10-hr fluorination at 450°C.

Studies have also shown[13] that the use of recycled fluorine is feasible in the direct fluorination of uranium oxide fuel, using Alundum as inert bed material, since oxygen does not exert a deleterious effect on plutonium retention in Alundum. The use of Alundum for more than a single fuel loading may be limited not only by the accumulation of fission products but also by the increase of plutonium retention in the Alundum with reuse of the bed material. After the reuse of Alundum in five successive experimental fluorinations of mixed oxides (50 hr, 450°C), the plutonium concentration in the Alundum rose to approximately 0.1 per cent.

The effect of additives such as zirconium tetrafluoride, nickel fluoride, and fission-product elements on the plutonium retention in Alundum is being studied in laboratory-scale fluorination tests.[14] The presence of 0.5 wt.% zirconium tetrafluoride and 3 per cent nickel fluoride in Alundum did not result in greater retention of either uranium or plutonium upon fluorination of the mixed oxides at 450°C for 10 hr. Therefore the presence of these additives, which could result from fluorination of the reactor vessel or from the decladding step, would not be expected to interfere with plutonium removal.

Thermal Decomposition of Plutonium Hexafluoride. In the fluorination step of the direct fluorination process for oxide fuels, a mixture of uranium and plutonium hexafluorides will be evolved from the reaction vessel. It will be necessary to separate the mixture and to recover the components in pure form. Thermal decomposition of plutonium hexafluoride to nonvolatile plutonium tetrafluoride is being explored at ANL[14] as a means of accomplishing a separation of uranium and plutonium, starting with mixtures of uranium hexafluoride and plutonium hexafluoride. Efficient removal of plutonium from a flowing gas stream of uranium hexafluoride and plutonium hexafluoride was obtained by decomposing plutonium hexafluoride on a solid surface of plutonium tetrafluoride contained in a reactor at temperatures of 200 and 300°C. Poor removal was obtained at 150°C. The starting ratio of plutonium to uranium at each temperature was approximately 0.1. The ratio in the gas phase after 4 hr was 5×10^{-5} at both 300 and 200°C; but it was only 2.5×10^{-2} at 150°C after 10 hr. The resulting bed of plutonium tetrafluoride contained only 0.7 per cent uranium.

Fischer et al.[16] at Argonne have published the results of an investigation of the kinetics and mechanism of the decomposition of plutonium hexafluoride. Experimental results on the thermal decomposition were fitted to a rate equation assuming concurrent first and zero orders with respect to plutonium hexafluoride pressure. The first-order dependence can be attributed to the unimolecular, homogeneous decomposition of plutonium hexafluoride in the gas phase, and the zero-order dependence can be attributed to the simultaneous, heterogeneous decomposition of plutonium hexafluoride on the surface of plutonium tetrafluoride saturated by the chemically adsorbed gas. The experimental activation energies were 15.9 ± 1.5 kcal/mole

for the zero-order reaction and 19.6 ± 0.7 kcal/mole for the first-order reaction.

Corrosion of Nickel in Fluorine. Nickel is commonly employed as a construction material for process equipment in which fluorine is used as a reactant at elevated temperatures. The kinetics of the reaction of nickel with fluorine were studied[14] at temperatures from 300 to 600°C and at a fluorine pressure of 700 ± 25 mm Hg. Parabolic rate constants for high-purity nickel were 9.8, 81.0, 461, and 1860 (μg of F_2/cm^2 of nickel surface)^2/min at temperatures of 300, 400, 500, and 600°C, respectively. From these rate constants an activation energy of 17 kcal/mole was derived. The reaction rates obtained with nickel fluoride scale thickness up to 1×10^4 A were independent of fluorine pressure. The reaction rate during the initial period of the reaction appeared to be dependent on the grain size of the nickel sample; the smaller grain-size material had the greater rate of reaction. When fluorine was reacted with nickel already covered with a nickel fluoride scale of greater than 2.5×10^5 A, a dependence on fluorine pressure was noted. The continuing reaction for specimens having initial nickel fluoride scales of 2.5×10^5 A can be represented by an equation in which the rate is directly proportional to the 0.5 power of the fluorine pressure.

Properties of Volatile Fluorides

It has been established previously that uranium hexafluoride reacts with uranium tetrafluoride to form intermediate fluorides of various compositions. Nguyen[17] has reported a detailed study of the kinetics of the various reactions observed in the temperature range of 20 to 200°C. Michallet et al.[18,19] have prepared addition compounds of uranium hexafluoride and the fluorides of various trivalent and tetravalent metals. It was postulated that, since uranium and fluorine form several fluoride compounds of which certain ones may be considered the result of combinations of uranium ions in different states of oxidation, several addition compounds between uranium hexafluoride and metallic fluorides could be prepared. Using steric considerations, it was predicted that compounds of the type $MF_3 \cdot 0.562\ UF_6$ and $MF_4 \cdot 0.396\ UF_6$ should be formed. Compounds of these types were prepared at temperatures ranging from 125 to 620°C with fluorides of bismuth, iron, aluminum, tin, lead, thorium, and titanium. No addition compounds of divalent metals were prepared, except in those instances where the metal was capable of existing in a valence greater than 2.

Pyrometallurgical Processes

Pyrometallurgical processes are under development in the anticipation that processing economies will result from the capability of such processes for handling short-cooled fuels with an attendant reduction of fuel inventories, from the avoidance of chemical conversions, and from the general simplicity of the processes. Development of these processes has accompanied the development of fast reactors. The high-fissionable-material content of the fuels for fast reactors and the necessity of processing the fuels many times before complete fuel consumption is realized makes necessary the development of simple, economical processes for such fuels. Pyrometallurgical processes are, in general, not high-decontamination processes, and their development must therefore be accompanied by the development of methods for remote refabrication of reactor fuel elements.

Melt Refining

The first large-scale testing of pyrometallurgical processes will be conducted in the fuel-cycle facility (shown in the previous Review)[6] which has been built adjacent to the Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station in Idaho. The melt-refining process, a simple melting process in which fission products are removed by volatilization and selective oxidation reactions, will be employed initially for the recovery of discharged EBR-II fuel.

Laboratory demonstrations of the melt-refining process using highly irradiated EBR-II prototype fuel are being conducted at ANL[14] to provide confirmation of earlier results obtained with inactive and low-activity alloys and to observe any effects peculiar to high-burnup, short-cooled fuel. The principal objectives of a fourth experiment of this series were to identify the nature and quantity of fission-product activity retained by the zirconia melt-refining crucible and to establish material balances for important elements. Material-balance and distribution data

in Table III-1 show no preferential distribution of uranium, plutonium, and molybdenum between the ingot and skull material within the limits of analytical accuracy. Zirconium distributed with a slight preference for the skull material. The rare earths, yttrium, and tellurium were largely concentrated in the skull. Substantial amounts of barium, strontium, and cesium were found in the crucible material. These results are in agreement with tracer-level studies that showed substaintial penetration of the crucible by these elements. Appreciable cesium volatilization, also predicted by tracer studies, accounts for the low material balance for this element.

It is planned to maintain a reasonably inert argon atmosphere in the processing cell of the EBR-II fuel-cycle facility. However, depending on the inleakage rate of air into the cell and the rate of replacement of argon required by losses and processing operations, the nitrogen concentration in the argon cell gas may attain values as high as 5 per cent. Consequently the nitridation rates of irradiated EBR-II fuel pins is of considerable interest. Data from three runs[20] with irradiated pins of varying specific activity show a correlation of nitridation rate with specific activity. However, the rate differences may be associated with secondary effects of pin irradiation, such as an increase in surface area resulting from surface roughening. The nitridation rate of unirradiated fuel pins at 300°C remained constant as the nitrogen concentration of the argon was varied[20] from 2 to 100 per cent.

Table III-1 MATERIAL-BALANCE DATA FOR HIGH-ACTIVITY-LEVEL MELT-REFINING EXPERIMENT[14]

[Charge, 364.2 g of EBR-II Type Fuel (U–5 wt.% Fissium); Burnup, 0.87 Per Cent of Total Atoms; Cooling Time, 35 Days; Activity Level, 8.9 Curies per Gram of Fuel; Experimental Conditions, 1 Hr at 1400°C; Zirconia Crucible; Argon Atmosphere]

Constituent	Distribution (% of charge)			
	Ingot	Oxidized skull	Crucible	Total
Total metal	73.6	26.4*		100
Uranium	74	24		98
Plutonium	64	22		86
Molybdenum	77	24		101
Total rare earths and yttrium	1	67	16	84
Tellurium	1	66	6	73
Zirconium	66	33		99
Barium and strontium	0	23	73	96
Cesium	0		36	36
Total gamma	65	33	6	104
Total beta	13	56	21	90

*Obtained by difference.

A series of articles[21–25] has recently been published on the development of the remote refabrication procedures for EBR-II fuel. These include a discussion[21] of the engineering considerations involved in remote refabrication of lightly decontaminated fuel at high background radiation levels, 10^3 to 10^7 rads/hr. Among the engineering problems that arise are those resulting from radiation damage to lubricants, electrical insulation, elastic seals, and protective coating; fission-product heating; and the necessity of conducting operations in an oxygen-free inert-gas environment to prevent excessive oxidation of the fuel material. In a current program at ANL for testing various radiation-resistant lubricants, one grease, NRRG-159, a product of the Standard Oil Company of California, continued to perform satisfactorily after an accumulated exposure[20] of 4×10^9 rads, which is equivalent to four years of actual operating time in the fuel-cycle facility.

A description has been given of the injection-casting procedure developed for remote refabrication of EBR-II fuel pins.[22] In this procedure, inert-gas pressure is used to force molten alloy into thoria-coated, precision-bore, high-silica glass molds. In an experimental injection-casting furnace (see Fig. III-4), 16,000 fuel castings (0.44 in. in diameter and 15 to 18 in. long) for the first EBR-II core were produced in batches of 120. Another report is also available on the casting of EBR-II fuel pins and on the development of the injection-casting furnace.[26]

After the injection-casting operation, the fuel pins are processed and inspected by a series of operations that are performed semiautomatically.[23] The castings are first stripped from the molds by a device that breaks the molds and then are sheared to length (14.22 in.) and inspected. An air gauge, balance, length comparator, and eddy-current probe provide progressive measurements of diameter, weight, length, and internal quality. The accuracy of diameter, weight, and length measurements is 0.0002 in., 0.1 g, and 0.01 in., respectively.

Each EBR-II fuel pin is placed in a stainless-steel jacket tube together with bonding sodium, and a top closure is made by welding. A weld leak-detection system was developed based on

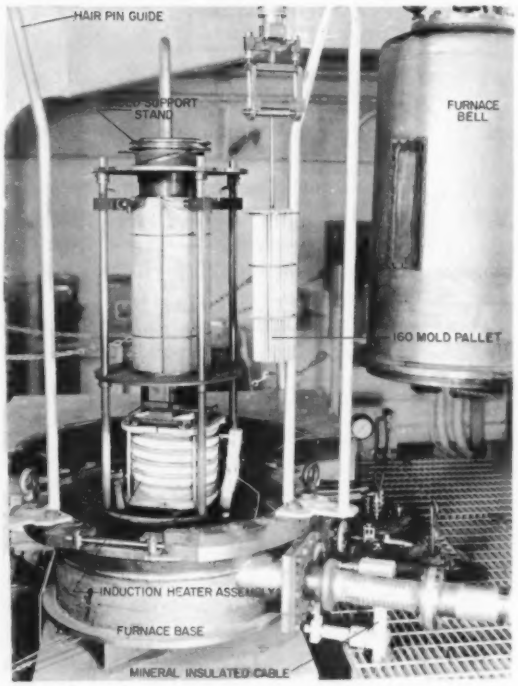

Fig. III-4 Prototype casting furnace.[22]

pressure decay in a miniature pressure chamber.[24] The sensitivity of leak detection is about 5×10^{-6} standard cubic centimeters of helium per second.

The sodium-bonding and bond-testing operations on canned EBR-II fuel pins have been discussed by Cameron and Hessler.[25] Acceptable sodium bonding was consistently realized at 500°C in an impact bonding machine in which the pins were bounced about $1\frac{1}{2}$ in. by impacts from underneath for a total of 1000 impacts. The integrity of sodium bonds was determined nondestructively by use of eddy-current coils that were found capable of detecting voids smaller in diameter than the maximum permissible of $\frac{1}{16}$ in. Liquid-sodium levels within the fuel-pin cans were determined by X-ray techniques with an accuracy of $\pm\frac{1}{64}$ in.

General Information Related to Melting of Uranium and Thorium. Two papers[27,28] concerning uranium metal quality as affected by melting and casting conditions have been published[29] in the *Transactions of the Vacuum Metallurgy Conference, 1960.* In one of these the effect of pressure on uranium ingot chemistry and metal quality is described.[27] Developments that have improved the fuel-core quality and reduced the production costs are discussed in the other.[28]

Various refractory oxide coatings on graphite crucibles were investigated for the induction melting of thorium and thorium-uranium alloys.[30] The effectiveness of a coating was measured by the extent of crucible attack and the degree of carbon contamination of the casting. Best results were obtained with wash coatings of yttria and zirconia and a flame-sprayed zirconia coating. Thoria was unsuitable as a coating, and beryllia required additional investigation. Procedures have also been described for the vacuum induction casting of uranium-molybdenum alloys into long and thin plates, such as might be required for reactor fuel elements.[31]

Fundamental Studies of Liquid-Metal and Salt Solutions

Solubilities in Liquid-Metal Systems. Knowledge of solubility relations is necessary for the design of fuel processes. Recent additions to the growing fund of solubility data are the solubilities as a function of temperature of krypton in liquid cadmium and indium;[32] praseodymium and beryllium in liquid zinc;[20] uranium in liquid indium;[20] vanadium,[1] osmium,[1] aluminum,[33] and rhenium[33] in liquid bismuth; and iron[33] and cobalt[33] in mercury. An equilibrium diagram for the lead-zinc system, based on recent measurements of mutual solubilities at temperatures above 650°C, has been presented.[2]

The liquidus curves of the uranium-zirconium-bismuth system have been reported[34] at several temperatures between 350 and 425°C, together with hypotheses of the nature of the phase diagram.

Nature and Thermodynamic Properties of Metals and Thermodynamic Compounds. The utility of solubility measurements is increased considerably when the solid phase in equilibrium with the saturated melt is identified and characterized. By recording effusion-balance measurements, a series of intermetallic phases in the lanthanum-cadmium system was identified[20] as follows: $LaCd_{11}$, La_2Cd_9, $LaCd_{\sim 8}$, $LaCd_2$, and LaCd. The decomposition pressure of UCd_{11}, the only intermediate phase in the uranium-

cadmium system, has also been measured by means of a recording effusion balance,[35] from which measurements the free energy, standard heat, and entropy of formation of UCd_{11} were calculated. The free energy, enthalpy, and entropy of formation of USn_3 have been determined by electromotive-force measurements.[20]

In a continuing program at Mound Laboratory, the physical properties of various metals associated with reactor fuel systems are being determined. The liquid densities of cerium, lanthanum, and praseodymium have recently been reported.[36] Viscosity and interfacial tension measurements are in progress on various liquid-metal systems, among these being various plutonium alloys that have possibilities as reactor fuels.[36]

Measurements of the densities of both liquid uranium and liquid plutonium have been reported. The density of liquid uranium from its melting points of 1406 to 1900°K may be represented by the equation D_{liq} $(g/cm^3) = 19.356 - 10.328 \times 10^{-4}T$ (°K) with a probable error[37] of ±0.078 per cent. It was concluded that the density of uranium is a straight-line function of temperature far beyond the metal's normal boiling point. From the tabulated data, liquid densities of pure U^{233}, U^{235}, and U^{238} can be calculated. The density of liquid plutonium, determined by pycnometric technique,[38] may be represented by the equation D_{liq} $(g/cm^3) = 17.63 - 1.52 \times 10^{-3}T$ (°C) with an accuracy of ±0.04 g/cm^3.

The following publications of general interest have been issued:

1. *Plutonium and Its Metallurgy*,[39] a discussion of various physical properties of plutonium and its application as a plutonium fuel
2. *Plutonium 1960*,[40] the proceedings of the Second International Conference on Plutonium Metallurgy
3. *The Metal Plutonium*,[41] a collection of 35 papers presented at the 1957 World Metallurgical Congress in Chicago
4. *The Metallurgy of Beryllium*,[42] the main findings and conclusions of 70 papers presented at the 1961 International Conference on the Metallurgy of Beryllium
5. *The Temperature Dependence of the Viscosity of Metals*,[43] an attempt at a general correlation whereby liquid-metal viscosities at particular temperatures may be calculated using the atomic weight, atomic volume, and melting temperature

Distribution of Elements Between Immiscible Phases. Studies of the distribution of fissionable and fission-product elements between immiscible phases are being made to evaluate solvent-extraction possibilities. Equilibrium studies between molten-metal and -salt systems are under way at Ames Laboratory. Recently the distributions of rare-earth elements and yttrium have been measured[44] at 600°C and at 700°C between zinc-magnesium alloys and a potassium chloride–lithium chlo-

Table III-2 DISTRIBUTION OF RARE EARTHS AND YTTRIUM BETWEEN A MOLTEN POTASSIUM CHLORIDE–LITHIUM CHLORIDE–MAGNESIUM CHLORIDE SALT AND A MOLTEN MAGNESIUM-ZINC ALLOY[44]

(Salt Phase: KCl-LiCl Eutectic Plus $MgCl_2$ to 15 wt.% Concentration; Metal Phase: About 3 wt.% Magnesium in Zinc)

Distributing element	Temp., °C	Salt-phase concentration, wt.%		Metal-phase concentration, wt.%		
		Distributing element	Mg	Distributing element	Mg	K_N*
Neodymium	700	0.015	3.75	0.72	2.64	78
Neodymium	600	0.005	3.94	0.54	3.44	133
Yttrium	700	0.19	3.78	0.63	2.39	7
Yttrium	600	0.035	3.83	0.30	2.49	20
Cerium	700	0.046	4.79	0.87	0.67	351
Cerium	600	0.0045	3.92	0.50	2.50	280
Samarium	700	0.75	3.88	0.032	2.73	0.07
Samarium	600	0.68	3.62	0.042	2.99	0.08

*$K_N = \left(\frac{\text{wt.\% } M_m}{\text{wt.\% } M_s}\right)\left(\frac{\text{wt.\% } Mg_s}{\text{wt.\% } Mg_m}\right)^{2/3}\left[\frac{(w/n)_s}{(w/n)_m}\right]^{1/3}$ where s and m refer to salt and metal, respectively, and w/n refers to an average molecular weight.

ride eutectic salt containing 15 wt.% magnesium chloride. For the reaction of interest,

$$MCl_3 + {}^3/_2Mg \rightarrow M + {}^3/_2MgCl_2$$

the equilibrium constant may be expressed as $K = K_N K_\gamma$, where K_N is the mole-fraction ratio of products over reactants and K_γ is the corresponding activity-coefficient ratio. In the absence of activity-coefficient information, results have been expressed in terms of K_N, which is defined in the footnote of Table III-2. Results in Table III-2 show effective reduction of neodymium, cerium, and yttrium from the salt phase, with reductions being slightly more complete at 600°C than at 700°C. Samarium remained largely in the salt phase, as would be expected from the large negative free energy of formation of samarium dichloride.

Measurements of the distribution coefficients of plutonium, uranium, rare-earth elements, and yttrium at 800°C between pure magnesium chloride and magnesium-zinc alloys as a function of magnesium concentration are under way at ANL[20] in the hope that a separation of uranium and plutonium from rare earths and yttrium can be achieved by fused-salt extraction. Distribution data shown in Fig. III-5 result in a family of curves that show considerable dependence on the magnesium concentration in the metal alloy. Considerable difference is apparent between the rare-earth-element distribution coefficients[20] and those of uranium[45] and plutonium,[45] indicating considerable separation potential by fused-salt extractions. In agreement with the above Ames data, samarium remained essentially completely in the salt phase. The two uranium curves in Fig. III-5 were obtained in two separate experiments in which the uranium concentration differed by a factor of 10 (highest in upper curve). No such concentration dependence was found for the rare-earth elements. The effect of concentration on the plutonium distribution has not been investigated.

Continuous countercurrent liquid metal–liquid salt extractors are under development. Burkhardt and Josephson have recently described[46] a countercurrent molten salt–metal contactor, a modified disk-doughnut type, in which stage efficiencies of up to 37 per cent were obtained at 350°C in the extraction of cadmium from bismuth by a potassium chloride–zinc chloride eutectic. The kinetics of fused

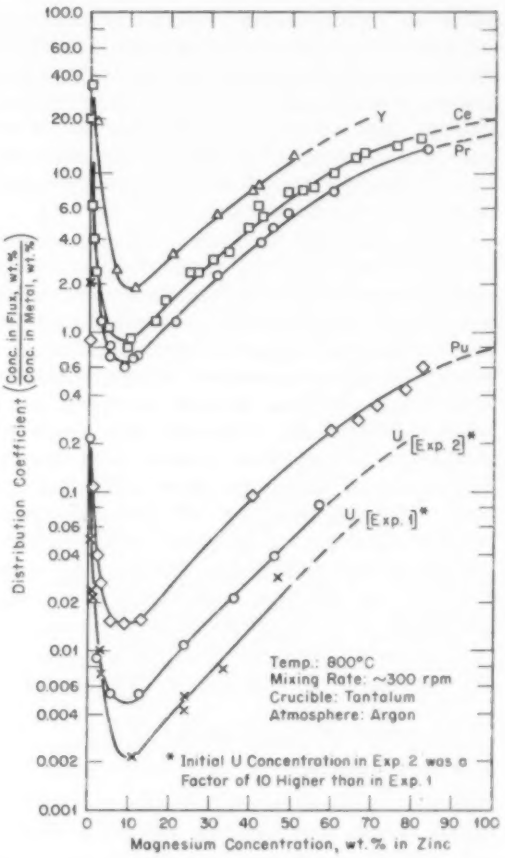

Fig. III-5 Distribution of selected elements between zinc–magnesium alloys and magnesium chloride.[20]

salt–liquid metal extractions are also under study at Brookhaven National Laboratory using a sodium chloride–potassium chloride–magnesium chloride eutectic as the salt phase and a dilute solution of magnesium and zirconium in bismuth as the metal phase, with cerium as the distribution solute. Work is being carried out in a 4-in.-ID by 42-in.-long disk-and-doughnut column. At the present time axial mixing experiments are being conducted.[1,33]

Reduction of Compounds in Liquid-Metal Systems. The reduction of compounds, particularly those of uranium, thorium, and plutonium, is necessary in several pyrometallurgical processes. In the preceding Review,[6] considerable information was presented on the reduction of uranium and thorium oxides by magnesium in zinc–magnesium–molten salt systems. Contin-

uation of work at ANL[20] on the reduction of thorium dioxide by zinc-magnesium solutions shows that effective reduction occurs within a limited composition region of the calcium chloride–magnesium chloride–calcium fluoride flux system. This region lies above 50 mole % magnesium chloride and between 7 and 15 mole % calcium fluoride.

The preparation of high-purity rare-earth metals by reduction of purified halide salts with calcium or lithium has been achieved in high yield by inert-atmosphere, crucible reduction techniques.[47] Bomb reduction techniques were generally unsuccessful. Vacuum reduction techniques, i.e., the Pidgeon process, were found to be readily adaptable to commercial production of rare-earth metals from oxides. Reductions of europium oxide by lanthanum with yields in excess of 90 per cent were realized at temperatures as low as 900°C.

Lithium and a calcium-lithium alloy were found to be efficient reductants of yttrium trifluoride in a metallothermic, intermediate alloy process.[48] Magnesium, sodium, aluminum, and zinc were less satisfactory reducing agents.

Development of Liquid-Metal and Salt Processes

Several fuel-recovery processes utilizing molten metals and salts as processing media are under development. At ANL development has been continued on a skull reclamation process for reclaiming uranium from crucible residues (skull material) of the melt-refining process and of a process for concentrating plutonium bred in the EBR-II blanket material. The principles of both processes have been fairly well established,[49] and increasing attention is now being given to engineering aspects.[20]

Considerable effort has been devoted to perfecting and demonstrating the various phase separations encountered in the skull reclamation and blanket processes. Because experience has shown that pressuring liquid phases out through dip tubes (a method called pressure siphoning) is a very expedient procedure and readily adaptable to remote operation, this method has received principal attention. A dual transfer tube unit has been developed by which clean separation of molten-flux and -metal phases has been repeatedly demonstrated without requiring knowledge of the interface location.[20] Consistent removals of supernatant liquid-metal phases from precipitated uranium phases in excess of 90 per cent have been demonstrated.[20]

Small-scale demonstrations of both the skull reclamation and blanket processes are currently under way.[20] Plans are now being made for scaleup of the processes to about a 2.5-kg uranium batch size. Subsequently, it is planned to install these processes in the EBR-II fuel-cycle facility.

An improved technique for electrorefining thorium into molten zinc at 600°C has been reported.[50] It was suggested that such an electrorefining step might constitute the initial step of a process for the low decontamination of nuclear fuels or reactor breeder blankets containing thorium. The use of a molten-zinc cathode eliminates the difficulties of loosely adherent, salt-laden, dendritic deposits encountered with solid inert electrodes. The zinc may be subsequently removed from the thorium-zinc alloy by vaporization. Current efficiencies of essentially 100 per cent were obtained with a lithium chloride–potassium chloride salt batch containing 15 wt.% thorium tetrachloride and at current densities of up to 0.53 amp/cm^2 at the cathode and 2.33 amp/cm^2 at the anode. The current efficiency was markedly improved by stirring the zinc. The practical limit for the deposition of thorium into zinc at 600°C is about 15 wt.% thorium, at which concentration the alloy becomes pastelike and difficult to stir. It is possible to obtain this high concentration, even though the solubility of thorium in zinc is only of the order of 1 per cent, because of the formation of Th_2Zn_{17}, which precipitates.

A second progress report has been issued on the separation of uranium from thorium by molten-magnesium extraction.[51] The process shown in Fig. III-6 is aimed at separation and recovery of thorium from a thorium breeder blanket. It consists of dissolution of thorium in magnesium, in which solution the uranium has very low solubility and precipitates. In the experimental work the supernatant thorium solution was removed by filtration, and the uranium residue was further concentrated by vaporization of the magnesium and then consolidated by arc melting. Most of the thorium in the filtrate was precipitated as the hydride, which was decomposed after removal of the supernatant solution by filtration, and the thorium was recovered in the same manner as that used for

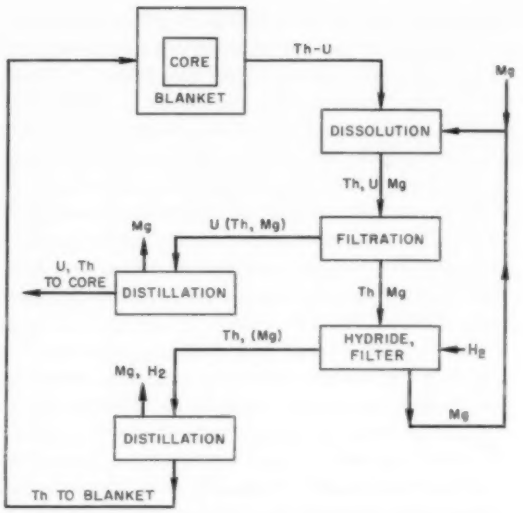

Fig. III-6 Separation of uranium from thorium by magnesium extraction.[51]

the uranium fraction. The supernatant solution from the thorium hydride precipitation step, which contains about 25 per cent of the thorium, is recycled to the dissolution step.

Uranium recoveries in a thorium-uranium concentrate in excess of 90 per cent were shown, but the bulk of the recoveries ranged between 70 and 90 per cent. The unrecovered uranium would not be lost, however, since it would be recycled with either the thorium or magnesium. Thorium-to-uranium ratios of around 1:1 were realized in the best experiments. Fission-product behavior was discussed. A silver-magnesium alloy was also briefly investigated as a processing medium and showed some promise, but the removal of silver, which has fairly low volatility, from the product phases gave problems.[51]

Construction Materials

The success of pyrometallurgical processes under development and the feasibility of molten reactor fuels are dependent on the availability of suitable container materials. After 8000 hr of operation at 480 to 575°C, the first Los Alamos Plutonium Reactor Experiment (LAMPRE-I) core loading (a plutonium-iron eutectic alloy) was permitted to freeze.[52] Dissected tantalum corrosion capsules from the core showed no evidence of penetration, which corroborates out-of-reactor tests. The impurities present in the fuel and plutonium monocarbide added as a corrosion preventative tended to segregate at the interface and impeded fission-gas disengagement, thereby causing frothing and physical displacement of the fuel. Improved corrosion performance has been realized with a high-purity iron-eutectic alloy to be used for the second core loading[52] of LAMPRE-I. The improved performance is mainly attributed to a very low calcium-magnesium content (below 5 ppm) of the fuel alloy. Equally satisfactory performance for containing this second core loading at temperatures up to 675°C has been realized with high-purity electron-beam-melted unalloyed tantalum; arc-melted unalloyed tantalum; electron-beam-melted tantalum containing 0.1 per cent tungsten; and a tantalum alloy containing 0.75 wt.% tungsten and 0.2 wt.% yttrium.

In higher temperature (750°C) tests, the effect of plutonium concentration in a plutonium-cerium-cobalt alloy system on corrosion of unalloyed tantalum was examined.[52] The corrosion by dilute plutonium alloys (below 5 g of plutonium per cubic centimeter) was close to that acceptable for experimental reactor use. Fortunately this area of concentration is of interest for high-performance fuels. Attack of tantalum at 750°C became very severe as the plutonium concentration was increased to 15 g/cm^3. Screening tests are also reported for other fuels and other container materials.

The long-term corrosion resistance of materials to boiling and superheated mercury and sodium is under investigation at Brookhaven[1,33] since these materials are of great interest as turbine-driving fluids for nuclear satellite power plants. Corrosion of carbon steel by boiling mercury was observed in both titanium-inhibited and noninhibited systems. Refractory metals (tantalum, tungsten, molybdenum, and columbium–1 per cent zirconium) were not attacked by mercury in a reflux capsule test operated for 3000 hr at 1100°F. Tests to determine the corrosion resistance of columbium and tantalum and their alloys to sodium are just being started.

The suitability of tantalum, molybdenum, and beryllium for containment of liquid bismuth in a liquid-metal-fuel reactor has been studied in laboratory capsule tests.[53] All three materials had adequate corrosion resistance at 750 and 975°F.

Development of Equipment and Techniques

Reference was previously made, in the section on "Distribution of Elements Between Immiscible Phases," to the development of countercurrent contacting equipment for immiscible molten metals and salts.[1,33,46] The development of a device for effecting molten salt–molten metal phase separations[20] was briefly discussed in the section on "Development of Liquid-Metal and Salt Processes."

Experience in liquid-metal handling techniques is being gained at ANL through long-term operation of a large cadmium distillation unit. Information, in addition to that on metal distillation, is being obtained on liquid-metal transfer, liquid-level detection, pressure and temperature measurement and control, and control of volatilized metal vapors in processing equipment. Operation of this equipment, described in a previous Review,[49] was recently resumed after installation of a new induction heating coil. Over 600 kg of cadmium has been distilled in three runs at rates of up to 40 kg/hr. The equipment is performing very satisfactorily.

Other Nonaqueous Processes

Pyrochemical processing procedures, which are being applied principally to oxide and carbide reactor fuels, generally utilize gases, molten salts, and liquid metals as reagents and reaction media. They resemble pyrometallurgical processes in the use of high temperatures, in a capability for handling short-cooled fuels, and in simplicity and compactness. Since only moderate fission-product decontamination is realized in both types of processes, they are usually integrated with remote fuel-fabrication procedures to form a complete fuel cycle.

Oxide Fuel Processing

The salt-cycle process, under development at Hanford, is an electrolytic procedure for processing irradiated uranium oxide–plutonium oxide fuels.[54–56] The mixed oxide fuel is first dissolved in a molten-chloride-salt bath by sparging the mixture with chlorine or hydrogen chloride. A portion of the uranium in solution in the form of uranyl ion is reduced electrolytically to the dioxide, which is essentially free of plutonium and is a by-product of the process. The plutonium and remaining uranium are then codeposited as the dioxides. This latter product is thereby sufficiently enriched in plutonium that it can be recycled to the reactor. Alternative methods of separating uranium, plutonium, and fission products are also being examined.

Recent experimental results have shown that plutonium dioxide can be precipitated from a molten-salt solution of uranium, plutonium, and rare earths by sparging a melt of the proper composition with a mixture of oxygen and chlorine. Under these conditions a good separation from uranium and rare earths is achieved since these elements remain in solution. It is further possible to electrodeposit uranium dioxide from a melt of the same composition with a good separation from plutonium and rare earths. No satisfactory means have been found thus far, however, for effecting a good rare-earth separation during electrolytic codeposition of uranium dioxide and plutonium dioxide.[55]

The precipitation of plutonium dioxide by sparging the salt solution with an oxygen-chlorine mixture is affected strongly by the compositions of the melt and the sparge gas.[55] This reaction was investigated at 575°C, using three salt systems of the following compositions: 2.6 LiCl–NaCl, 2.6 LiCl–KCl, and LiCl-KCl. Each melt contained 9.2 wt.% uranium and sufficient plutonium and rare earths to give uranium-to-plutonium and uranium-to-rare earth ratios of 100 and 1000, respectively. In the 2.6 LiCl–NaCl system, the best results were obtained with a 28 per cent oxygen–72 per cent chlorine mixture. Eighty-six per cent of the plutonium was converted to oxide, and 82 per cent was recovered by settling and decantation. Decontamination factors based on plutonium were 370 for Pm^{148} and 1500 for uranium. Increasing the oxygen content of the sparge gas resulted in a greater tendency for uranium and rare earths to be carried by the plutonium dioxide precipitate. In the 2.6 LiCl–KCl system, a 55 per cent oxygen concentration in the sparge gas converted 90 per cent of the plutonium to the oxide. The precipitate was finely divided, however, and only about 50 per cent was recovered. No precipitation occurred in the LiCl-KCl melt with 55 per cent oxygen or in the 2.6 LiCl–KCl melt with 28 per cent oxygen in the sparge gas.

Plutonium dioxide has also been precipitated from chloride media through metathesis of dis-

solved plutonium chloride by stannic oxide.[54] In the 2.6 LiCl–NaCl system sparged with chlorine at 575°C, 1 g of stannic oxide precipitated 45 mg of plutonium to give a 90 per cent recovery. The presence of 10 wt.% uranium had no influence on the plutonium recovery. In two experiments, decontamination factors based on plutonium were 90 and 260 for promethium tracer and 150 and 1500 for uranium.

Plutonium and rare-earth decontamination was investigated during the electrodeposition of uranium at 600°C in the 2.6 LiCl–NaCl system. With chlorine sparging, partition electrolysis resulted in plutonium and promethium decontamination factors[55] of 85 and 1500. Attempts to codeposit uranium and plutonium oxides by adding oxygen to the sparge gas so as to precipitate plutonium dioxide during electrodeposition of uranium dioxide did not yield encouraging results.

Further crystal-growth studies of uranium dioxide electrolyzed from various molten-salt systems have been reported.[54–56] In molten LiCl-KCl, uranium dioxide crystals weighing as much as 1.5 g have been produced, with oxygen-to-uranium ratios as low as 2.005 and impurity levels of <20 ppm potassium and <5 ppm lithium. Agitation proved to have no effect on the crystal growth. Time-lapse photographs of uranium oxide deposits from $PbCl_2$–2.5 KCl show that the initial deposits are needles that grow rapidly on the 1 1 0 and 1 1 1 faces and gradually convert to cubes on the 1 0 0 faces at the tips of the needles. The 2.6 LiCl–NaCl system suffers from the disadvantages of difficulty in drying the melt at the 600°C minimum operating temperature. Scouting studies with sulfate and fluoride melts resulted in porous, low-quality deposits. A single experiment at 750°C with NaCl-KCl containing 5 wt.% sodium fluoride, however, produced dense crystals with an oxygen-to-uranium ratio of less than 2.01.

Chemical investigations of the oxidation kinetics of lower oxidation state uranium to U(VI) in molten-salt solution during air sparging have been reported.[54–56] Solutions containing up to 1 wt.% uranium were prepared by four methods believed to produce U(IV):

1. UO_2 (suspended in melt) + HCl(g)
2. UO_2Cl_2 (solution) + HCl(g)
3. UO_2Cl_2 (solution) + C(s) + Cl_2(g)
4. Dissolution of Cs_2UCl_6 in melt

The resulting melts were sparged with air at 600°C, and the amount of reduced uranium, measured as U(IV), was determined as a function of time. In the melts used (LiCl-KCl, KCl–3 LiCl, and NaCl–3 LiCl), it appears that reaction 2 above results in two species of uranium in the lower oxidation states, one species being more easily oxidized by the air sparge than the other. The relative amounts of the two species varied with the melt. Reaction 1 produced two species of lower oxidation state uranium when U(VI) was present in the melt, but only one species in its absence. Reactions 3 and 4 produced only one species, apparently the one that is less easily oxidized. It is suspected that the easily oxidized species may be U(V) or U(IV) oxychloride and that the more slowly oxidized species is U(IV) chloride.

Oxidation rates of U(IV) during sparging with air and with oxygen-chlorine mixtures at 600°C were compared in various melts.[56] With air sparging, the oxidation rate was zero order with respect to the U(IV) concentration, and complete oxidation occurred within $\frac{1}{2}$ hr. Slower oxidation took place with a 30 per cent oxygen–70 per cent chlorine mixture, especially at U(IV) concentrations below 0.3 wt.%. Complete oxidation required 1 to 2 hr, depending on the molten-salt system used.

Thermodynamic data have been derived from electromotive-force values for the reaction

$$UO_2(s) + Cl_2(g) = UO_2Cl_2 \text{ (solution)}$$

in NaCl-KCl at 670, 720, and 770°C and at uranyl chloride concentrations of 0.03 to 0.9 molal.[54] With a reference state of 1.0 molal uranyl chloride at 720°C, the oxidation potential is 0.550 ± 0.003 volt and the free energy change is -24.4 kcal/mole. Conversion to standard-state values is not yet possible since necessary data on a needed activity coefficient are unavailable.

The mechanism of the cathodic reduction of uranyl chloride in NaCl-KCl has been verified by refined capacitance versus potential measurements. The following two steps are observed: (1) $UO_2^{2+} + e^- = UO_2^+$, and (2) $UO_2^+ + e^- = UO_2(s)$.

Further engineering developments on the salt-cycle process have been described.[54–56] A microscale electrolytic reduction has proved useful in determining the dryness of the molten-chloride systems.[54] Chlorination at 700°C, followed by hydrochlorination at 600°C and pre-

electrolysis with graphite electrodes at 600°C, is an effective procedure for drying the melts. The importance of high-integrity equipment to prevent exposure to atmospheric moisture is stressed.[55] A 50-lb deposit of uranium dioxide with an oxygen-to-uranium ratio of 2.0036 was produced with 61 per cent current efficiency over 113 hr at 580°C. The product was of high quality. Other large-scale experiments showed that deposits of good quality cannot be assured if undissolved U_3O_8 is allowed to remain in the melt.[55]

Equipment development has included preliminary investigations of frozen-wall containers and demonstration of satisfactory agitation by means of a submerged gas-lift pump.[54,56]

A study has also been conducted at Harwell concerning the electrodeposition of uranium dioxide from solutions of uranyl chloride in NaCl-KCl eutectic.[57] The mechanism of this reaction is discussed in Sec. V of this Review.

Electrolytic procedures are also being considered at Hanford for the codeposition of uranium dioxide and thorium dioxide.[56] The first series of experiments involved solutions of uranyl chloride and thorium tetrachloride in molten KCl-LiCl between 500 and 700°C. It was concluded that solid solutions of at least 14 wt.% thorium dioxide in uranium dioxide can be formed as polycrystalline deposits. The oxide deposit can be enriched in thorium, as compared to the melt, by factors at least as high as 2 or 2.5. The degree of enrichment decreases with increasing thorium tetrachloride concentration in the melt.

Incorporation of thorium dioxide into the oxide deposit is believed to occur through the reaction of thorium tetrachloride with the uranium dioxide as it is deposited at the cathode:

$$ThCl_4 + UO_2 = ThO_2 + UCl_4$$

The Alloy Reguline Chloride Oxidation (ARCO) process, another procedure utilizing molten-salt media, has been demonstrated earlier as a method for dissolving metallic uranium, thorium, aluminum, and various refractory cladding metals such as stainless steel, chromium, niobium, and zirconium.[58] The possibility of extending the ARCO process to include uranium dioxide fuels has been investigated recently at Idaho.[59]

Uranium dioxide pellets weighing 5.8 g each were exposed to molten lead chloride under various conditions. In lead chloride alone, at 500 to 800°C, no appreciable reaction had occurred after 1 hr, suggesting the possibility that zirconium alloy cladding could be removed at 500 to 520°C with negligible dissolution of the uranium dioxide. When chlorine was passed through the melt, dissolution of the oxide occurred but at rates too slow for process use. On further addition of copper chloride to the melt as a catalyst, however, the rate increased by four to five orders of magnitude. Iron also proved to be an effective catalyst.

The dissolution rate is controlled by three factors in the system: (1) the copper concentration, (2) the flow rate of chlorine, and (3) the uranium dioxide surface area. When excess chlorine was available, the dissolution rate was directly proportional to the copper chloride concentration in the salt. During the course of the experiments, the oxide surface area was not ordinarily the rate-controlling factor. Since the reaction is not strongly temperature-dependent, feasible dissolution rates are possible at temperatures of 430°C or less.

As a laboratory demonstration, a segment of a Shippingport PWR fuel rod consisting of 10.4 g of uranium oxide clad with 6.2 g of zirconium was dissolved at 550°C in a melt containing 35 g of lead chloride and 1.4 g of copper. Chlorine was passed through the system at 110 g/min as the rod was immersed slowly in the melt. The zirconium was volatilized from the system as zirconium tetrachloride. The over-all reaction was completed within 4 hr with 44 per cent utilization of chlorine. The melt composition, when the dissolution was stopped, was 20.6 mole % uranyl chloride, 11.8 mole % copper chloride, and 67.6 mole % lead chloride. It is also likely that stainless-steel-clad fuels can be dissolved integrally, using the iron content of the alloy as the catalyst.

Further developments at Atomics International on the direct, low-decontamination processing of uranium dioxide fuels have been reported.[60–62] Only gaseous reagents are used in this process. The uranium dioxide fuel is alternately oxidized by air or oxygen at 200 to 600°C and reduced by hydrogen at 600°C until the particle size is reduced to a level suitable for refabrication. The procedure is used both to remove the solid fuel from stainless-steel

cladding and to effect the particle size reduction. Although some fission-product removal is realized (mainly noble gases, tellurium, and iodine), the primary objective is to facilitate reenrichment and refabrication of fuel elements for recycle to the reactor. Cold pressing and sintering are used in the refabrication.

Experiments are currently in progress with 100-g quantities of highly irradiated uranium dioxide. Material irradiated to 5700 and 15,000 Mwd/metric ton of uranium has been processed. The equipment that was used was developed for the remote refabrication and inspection of uranium dioxide fuel. The irradiated pellets were pressed, heated in hydrogen to 1750°C at a rate of 300°C/hr, and sintered for 10 hr. The resulting pellet densities were 80 to 94 per cent of the theoretical value. Although higher densities are desired, the demonstration of remote operations is considered satisfactory. The major factor affecting the sintered-pellet density is the previous history of the uranium dioxide powder. A minor factor is the binder solvent used. A differential thermal analysis technique is currently being applied as a means of characterizing the sinterability of the processed uranium dioxide powder.

The oxidation and reduction behavior of uranium oxides has also been investigated at the Japan Atomic Energy Research Institute in Tokyo, along with a study of the mechanism of xenon release during the reactions.[63]

Carbide Fuel Processing

At Atomics International, development of three low-decontamination procedures for processing uranium carbide fuels has continued.[60–62] The first process consists of oxidizing the carbide with oxygen or carbon dioxide at about 400°C to form uranium oxide, carbothermically reducing the oxide at or above 1300°C to regenerate the carbide, and arc-melting this material to form a solid product suitable for reuse as a fuel. The second process involves electrolytic dissolution of the carbide in a LiCl-KCl salt bath that deposits metallic uranium on a molybdenum cathode. The metallic deposit is dissolved in mercury and converted to carbide by reaction with propane as the mercury is removed by distillation. In the third approach the uranium monocarbide is converted to the nitride by reaction with nitrogen. The reaction is then reversed by heating the uranium nitride and carbon *in vacuo*. Only the electrolytic procedure produces significant fission-product decontamination. The other processes are essentially refabrication procedures.

Additional information has been obtained on the reaction of uranium monocarbide with nitrogen. Measurements of the reaction rate as a function of temperature show that it passes through a maximum at 850 to 900°C. The effect of particle size on the rate is relatively small. The product of the nitridation reaction is somewhat coarser than that obtained from oxidation of the carbide; sieve analyses show 80 to 90 per cent of the material to be in the −50, + 200 mesh fraction. The particle size of the product appears to depend on the extent of the reaction, with the particles becoming finer as the reaction approaches completion.

Ten experiments have been reported in which the nitridation reaction was reversed by heating the uranium nitride–carbon mixture *in vacuo*.[62] The results are shown in Table III-3. As the temperature was raised to 2000°C, the nitrogen content of the material decreased to 0.045 wt.%. At temperatures above 1500°C, the product was sintered, and at 2000°C it adhered to the graphite crucible.

Previous results had indicated that the reactivity of arc-melted uranium monocarbide toward oxygen, carbon dioxide, and nitrogen is increased by exposure to air saturated with water vapor.[6] The degree of activation has been correlated with the hydrogen content of the carbide, as determined by vacuum fusion analysis.[61] The nitridation rate of the carbide fuel, for example, varies exponentially with the hydrogen content (Table III-4). This effect, however, appears to be leveling off with time

Table III-3 REGENERATION OF URANIUM MONOCARBIDE BY HEATING URANIUM NITRIDE–CARBON MIXTURES IN VACUUM[62]

Time, hr	Temp., °C	Initial nitrogen content, wt.%	Final nitrogen content, wt.%
10	1300	7.7	2.63
8	1400	6.9	1.49
10	1500	7.3	1.10
5	1600	8.2	0.40
5	1600	6.7	0.28
10	1600	7.3	0.25
5	1800	8.0	0.20
5	1850	7.3	0.23
4	1900	8.0	0.036
4	2000	7.3	0.045

Table III-4 CORRELATION OF REACTIVITY AND HYDROGEN CONTENT OF "AGED" URANIUM MONOCARBIDE[61]

Age,* days	Time to 10% completion,† min	Hydrogen content, ppm
0	1050	0
3	715	1.5
7	273	6
14	44	9
22	9.4	13
29	6.4	17
42	4.5	19

*Exposure to air saturated with water vapor at room temperature.

†Reaction of uranium monocarbide with nitrogen.

of exposure at the longer times of 29 and 42 days. The carbon content of the uranium carbide also influences the degree of activation caused by exposure to water vapor.

Rate measurements of the conversion of uranium monocarbide to the oxide by carbon dioxide over the temperature range 375 to 500°C indicate first-order kinetics, i.e.,

$$\ln \frac{1}{1-x} = kt$$

where x is the fraction of carbide reacted at time t with an activation energy of 25 kcal/mole. Above 550°C the first-order rate law does not apply. Experimental determinations also show the rate to be proportional to the 0.3 power of the carbon dioxide pressure.

Several experiments have been reported in which 3 to 6 g of tracer-irradiated uranium monocarbide were arc-melted under various conditions.[61,62] Some fission-product removal occurred, but no correlation with time and power level could be made. High, low, and median decontamination factors for several fission-product elements are listed in Table III-5. Plutonium removals averaged 61, 73, and 78 per cent for melting times of 3, 6, and 9 min, indicating that some provision for plutonium collection will be necessary if arc-melting is used for the refabrication of uranium monocarbide.

The oxidation of uranium monocarbide by carbon dioxide, oxygen, nitrogen, and carbon monoxide has also been investigated at Harwell.[64] Sintered compacts were prepared by heating and sintering a mixture of uranium powder (−300 mesh) and carbon in the proper proportions. The final carbon content of the product was 4.75 to 4.85 per cent (the theoretical carbon content for UC is 4.80 wt.%). The measurements were made with a thermobalance in which the gas was passed over specimens 1.5 cm in diameter and 0.5 cm thick at a rate of 500 cm^3/min and at 1 atm pressure. The over-all reactions for the four gases are given as:

$$UC + 2CO_2 = UO_2 + C + 2CO$$

$$CO_2 + C = 2CO$$

$$3UC + 4O_2 = U_3O_8 + 3C$$

$$C + O_2 = CO_2$$

$$UC + N_2 = UN_2 + C$$

$$UC + 2CO = UO_2 + 3C$$

In all four cases the extent of the reaction proved to be linear with time. The reaction rates, shown in Table III-6, are approximately the same as the rates of the corresponding reactions of uranium metal under similar con-

Table III-5 FISSION-PRODUCT REMOVALS EFFECTED BY ARC-MELTING TRACER-IRRADIATED URANIUM MONOCARBIDE[61,62]

Fission product	Decontamination Factors		
	High	Low	Median
$Zr-Nb^{95}$	350	1	4
$Ce-Pr^{144}$	18	2	6
Ru^{103}	5	1	1.4
Cs^{137}	2000	37	1000
Sr^{90}	330	13	160
Total activity	8.6	1.4	3.4

Table III-6 REACTION RATES OF URANIUM MONOCARBIDE[64]

Gas	Temp., °C	Reaction rate for UC, mg of gas reacted/(cm^2)*(hr)
CO_2	500	2.4
CO_2	700	14
CO_2	850	56
CO_2	1000	185
O_2	350	1.4
N_2	700	0.96
N_2	850	46
CO	500	0.007−0.03
CO	600	0.007−0.05

*Geometric surface area of carbide.

ditions. For the higher density specimens, the activation energies at the lower temperatures are 15.5 ± 1.5, 25 ± 4, and 55 ± 10 kcal/mole for the reactions with carbon dioxide, oxygen, and nitrogen. In the case of carbon monoxide, an accurate value could not be determined, but it was not greater than 11 kcal/mole.

The reason for different rate laws obtained for these reactions at Atomics International[60–62] and at Harwell[64] is not clear. It is possible that it is related to the use of arc-melted material in the former case and sintered compacts in the latter.

References

1. J. H. Reynolds (Ed.), Nuclear Engineering Department Progress Report, May 1–August 31, 1961, USAEC Report BNL-696, Brookhaven National Laboratory, January 1962.
2. A. P. Litman, Corrosion of Volatility Pilot Plant Mark I INOR-8 Hydrofluorinator and Mark III L Nickel Fluorinator After Fourteen Dissolution Runs, USAEC Report ORNL-3253, Oak Ridge National Laboratory, Feb. 26, 1962.
3. A. E. Goldman and A. P. Litman, Corrosion Associated with Hydrofluorination in the Oak Ridge National Laboratory Fluoride Volatility Process, USAEC Report ORNL-2833, Oak Ridge National Laboratory, Nov. 15, 1961.
4. A. P. Litman and A. E. Goldman, Corrosion Associated with Fluorination in the Oak Ridge National Laboratory Fluoride Volatility Process, USAEC Report ORNL-2832, Oak Ridge National Laboratory, June 19, 1961.
5. *Reactor Fuel Processing*, 4(4): 32–35 (October 1961).
6. *Reactor Fuel Processing*, 5(2): (April 1962).
7. Oak Ridge National Laboratory, Chemical Technology Division Annual Progress Report for Period Ending May 31, 1961, USAEC Report ORNL-3153, Sept. 21, 1961.
8. *Reactor Fuel Processing*, 5(1): 30–35 (January 1962).
9. M. E. Whatley et al., Oak Ridge National Laboratory, Chemical Technology Division, Unit Operations Section, Monthly Progress Report, June 1961, USAEC Report ORNL-TM-34, Oak Ridge National Laboratory, Jan. 23, 1962.
10. D. O. Campbell and G. I. Cathers, Processing of Molten Salt Power Reactor Fuel, USAEC Report CF-59-2-61, Oak Ridge National Laboratory, Apr. 1, 1959.
11. *Reactor Fuel Processing*, 3(1): 21–22 (January 1960).
12. J. D. Gabor et al., Spray Fluorination of Fused Salt as a Uranium Recovery Process, USAEC Report ANL-6131, Argonne National Laboratory, March 1960.
13. Argonne National Laboratory, Chemical Engineering Division Summary Report, July, August, September 1961, USAEC Report ANL-6413, 1962.
14. Argonne National Laboratory, Chemical Engineering Division Summary Report, October, November, December 1961, USAEC Report ANL-6477, May 1962.
15. Argonne National Laboratory, Chemical Engineering Division Summary Report, April, May, June 1961, USAEC Report ANL-6379, October 1961.
16. J. Fischer et al., The Kinetics and Mechanism of the Thermal Decomposition of Plutonium Hexafluoride, *J. Phys. Chem.*, 65: 1843–1846 (1961).
17. Hoang-Nghi Nguyen, Contribution to the Study of the Intermediate Fluorides of Uranium, French Report CEA-1976, 1961.
18. M. Michallet, Contribution to the Study of the Reactions of Uranium Hexafluoride with Some Metallic Halides, French Report CEA-2110, 1961.
19. M. Michallet et al., Reaction of Uranium Hexafluoride with Some Metallic Fluorides, *Compt. rend.*, 253(25): 2980–2981 (Dec. 18, 1961) (in French).
20. S. Lawroski, Argonne National Laboratory, June 1962. (Unpublished)
21. A. B. Schuck and J. E. Ayer, *Nuclear Sci. and Eng.*, 12: 398–404 (1962).
22. H. F. Jelinek and G. M. Iverson, *Nuclear Sci. and Eng.*, 12: 405–411 (1962).
23. N. J. Carson, Jr., and S. B. Brak, *Nuclear Sci. and Eng.*, 12: 412–418 (1962).
24. A. P. Grunwald, *Nuclear Sci. and Eng.*, 12: 419–423 (1962).
25. T. C. Cameron and N. F. Hessler, *Nuclear Sci. and Eng.*, 12: 424–431 (1962).
26. H. F. Jelinek and P. L. Dewez, Casting of EBR-II Type Transient Test Elements and Equipment Development, USAEC Report ANL-6289, Argonne National Laboratory, September 1961.
27. R. B. Steck et al., in *Transactions of the Vacuum Metallurgy Conference, 1960*, pp. 109–117, New York Interscience Publishers, New York, 1961.
28. H. M. Eikenberry et al., in *Transactions of the Vacuum Metallurgy Conference, 1960*, pp. 101–108, New York Interscience Publishers, New York, 1961.
29. R. F. Bunshah (Ed.), *Transactions of the Vacuum Metallurgy Conference, 1960*, New York Interscience Publishers, New York, 1961.
30. N. H. Katz et al., Vacuum Induction Melting and Casting of Thorium and Thorium-Uranium Alloys, USAEC Report NAA-SR-5833, Atomics International, Oct. 30, 1961.
31. N. H. Katz and M. H. Binstock, Casting of Long and Thin Plates of Uranium-Molybdenum Alloys, USAEC Report NAA-SR-6227, Atomics International, Nov. 1, 1961.

32. G. W. Johnson, *Phil. Mag.*, 8(6): 943–946 (July 1961).
33. Brookhaven National Laboratory, March 1962. (Unpublished)
34. D. G. Schweitzer and J. R. Weeks, *Trans. Am. Soc. Metals*, 53: 259–264 (1961).
35. E. Veleckis et al., *J. Phys. Chem.*, 66: 362 (1962).
36. J. F. Eichelberger, Mound Laboratory Monthly Progress Report for August 1961, USAEC Report MLM-1118, Mound Laboratory, Aug. 31, 1961.
37. A. V. Grosse et al., *J. Am. Chem. Soc.*, 83: 4665–4666 (Nov. 20, 1961).
38. C. Z. Serpan, Jr., and L. J. Wittenberg, *Trans. Met. Soc. AIME*, 221: 1017–1020 (October 1961).
39. E. Grison, *Mém. sci. rev. mét.*, 58: 2–10 (January 1961).
40. E. Grison et al. (Eds.), *Plutonium 1960*, The Proceedings of the Second International Conference on Plutonium Metallurgy, Cleaver-Hume Press Ltd., London, 1961.
41. A. S. Coffinberry and W. N. Miner (Eds.), *The Metal Plutonium*, University of Chicago Press, Chicago, 1961.
42. The Metallurgy of Beryllium, *Nuclear Eng.*, 6: 531–533 (December 1961).
43. S. W. Strauss, *Nuclear Sci. and Eng.*, 12: 436–439 (March 1962).
44. A. F. Voigt, Newsletter for February, Ames Laboratory, March 1962.
45. J. B. Knighton, Argonne National Laboratory, private communication.
46. P. R. Josephson and and L. E. Burkhardt, *Trans. Am. Nuclear Soc.*, 4(2): 352 (November 1961).
47. T. T. Campbell et al., Preparation and Metallic Reduction of Rare-Earth Halides and Oxides, Report BM-RI-5880, Bureau of Mines, Albany Metallurgy Research Center, April 1960.
48. J. A. Haefling et al., A Study of Several Metals as Reductants for Yttrium Fluorides, USAEC Report IS-374, Ames Laboratory, September 1961.
49. *Reactor Fuel Processing*, 4(4): 45–46 (October 1961).
50. R. E. Johnson, Thorium Fused Salt Electrodeposition into a Molten Zinc Cathode, USAEC Report NAA-SR-6802, Atomics International, Jan. 15, 1962.
51. J. D. Chilton et al., Separation of Uranium from Thorium by Liquid Metal Extraction, Thorium Recovery and Fission Product Distribution, USAEC Report NAA-SR-6666, Atomics International, Feb. 1, 1962.
52. Los Alamos Scientific Laboratory, Quarterly Status Report on LAMPRE Program for Period Ending February 20, 1962, USAEC Report LAMS-2681, March 1962.
53. A. L. Lowe, Jr., *Corrosion*, 17: 475t–478t (October 1961).
54. W. H. Reas, Chemical Research and Development Operation Monthly Report, December 1961, USAEC Report HW-72142C, Hanford Atomic Products Operation, Jan. 15, 1962. (Classified)
55. W. H. Reas, Chemical Research and Development Operation Monthly Report, January 1962, USAEC Report HW-72590C, Hanford Atomic Products Operation, Feb. 15, 1962. (Classified)
56. W. H. Reas, Chemical Research and Development Operation Monthly Report, February 1962, USAEC Report HW-72902C, Hanford Atomic Products Operation, Mar. 15, 1962. (Classified)
57. R. S. Wilks, A Study of the Mechanism of the Electrolysis of UO_2Cl_2 in Molten NaCl-KCl Eutectic, Atomic Energy Research Establishment, Harwell, to be published.
58. H. T. Hahn and E. M. Vander Wall, Salt-Phase Chlorination of Reactor Fuels. I. Dissolution of Zirconium Alloys in Lead Chloride, USAEC Report IDO-14478, Phillips Petroleum Co., May 22, 1959.
59. E. M. Vander Wall et al., Salt-Phase Chlorination of Reactor Fuels. III. Catalyzed Dissolution of Uranium Dioxide in Lead Chloride–Chlorine Systems, USAEC Report IDO-14578, Phillips Petroleum Co., Feb. 5, 1962.
60. C. E. Weber, Atomics International, December 1961. (Unpublished)
61. C. E. Weber, Atomics International, January 1962. (Unpublished)
62. C. E. Weber, Atomics International, February 1962. (Unpublished)
63. S. Ichiba, The Behavior of Fission Product Rare Gases in the Change of Solid Phase. Oxidation and Reduction of Uranium Oxides, *J. At. Energy Soc. Japan*, 3: 705–710 (September 1961).
64. K. A. Peakall and J. E. Antill, Oxidation of Uranium Monocarbide, Atomic Energy Research Establishment, Harwell, to be published.

Section

IV

Reactor Fuel Processing

Waste Disposal

Evaluation of Containers for Sea Disposal

An evaluation of all types of containers currently used in sea-disposal operations was undertaken by AEC.[1-4] One phase of this study involved the testing at sea of some 150 actual disposal containers selected at random from waste packagers. The results of this study have been summarized in a previous Review.[1] The other phase involved a series of laboratory tests conducted by the Southwest Research Institute, San Antonio, Tex., to measure the effects of pressure and impact forces on various types of containers. The testing included containers with different thicknesses of pressure-resisting walls, the effects of different kinds of interior packing, various pressure-equalizing devices, and the ability of containers to resist the shock of striking the sea floor.

The test results revealed that, to have a reliable container system for sea disposal, certain fabrication considerations must be incorporated into the design. The incorporation of these design and fabrication details should provide sea-disposal containers that will not release radioactive wastes until the containers are deteriorated by the environment.

Four types of containers were considered in this study.[4] These were fabricated from steel drums and concrete and consisted of the following types: type I, a concrete shell of uniform thickness on the inside of a 55-gal drum; type II, a concrete shell of uniform thickness on the outside of a 55-gal drum; type III, a 55-gal drum with concrete bottom and top but with no cylindrical concrete shell; and type IV, a concrete shell that fills the volume between an inner fiber drum and an outer 55-gal steel drum.

The type I container (see Fig. IV-1), with reinforcement, performed the best with respect to structural behavior and containability. If this type of container is used, mechanical venting should be incorporated. However, all the container types studied proved to be satisfactory, if properly constructed. The container characteristics and fabrication details required to prevent the likelihood of serious container damage resulting from sea disposal are the same for all four container types. The design requirements to be fulfilled are as follows:

1. An adequate venting system must be provided to permit pressure equalization commensurate with container design.
2. A means must be provided to retain concrete-shell fragments in place, if the container is severely deformed, prior to coming to rest on sea bottom.
3. An adequate thickness of concrete shell to resist loads of packaging, handling, and sea disposal must be provided.
4. All unvented voids should be filled with concrete to eliminate the possibility of local buckling or rupture.
5. Contents should not be compressed so highly that they will spring back when restraint is released, or compressed to a volume that will become greater than the void volume when the contents are in contact with water.

The necessity for adequate venting of the contents was clearly demonstrated by the behavior of type I containers. This group consisted of containers which were naturally vented by concrete porosity and shrinkage cracks but which were without mechanical venting. The containers that were adequately vented by the shrinkage cracks and porosity suffered no damage, but the containers that were not adequately vented by natural means were damaged to a degree dependent on other fabrication

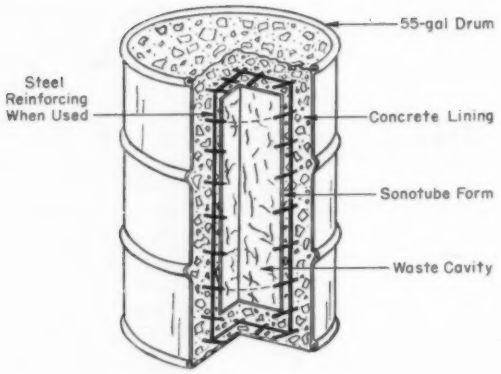

Fig. IV-1 Type I container for sea disposal.[4]

details. If no mechanical venting is provided, a container should be strong enough to withstand the external pressure to which it may be subjected, even though some natural venting action can occur as a result of the porosity and cracks in the concrete. No container was fabricated that was leakproof and could withstand the maximum test pressure (2700 psig). It seems unlikely that leakproof containers could be routinely fabricated from ordinary concrete, without the use of special construction details, because of the cracking that normally develops in concrete as a result of changes in moisture content and temperature during cure and storage; nor would concrete which did not crack be desirable, since the added factor of safety due to natural venting would be lost. This would be a very important consideration in the event that a stoppage should occur in the mechanical vent. The tests also indicate that completely dependable venting can be achieved only by incorporation of a vent tube. A ½-in. tube, open or crimped, will provide adequate venting if the permeability of the contents permits flow throughout the contents. These tests also demonstrated that waste material will not flow out of such vent tubes unless the external pressure is reduced below the internal pressure of the container.

The utility of providing a means for knitting or keeping the concrete fragments together, in case of container rupture, was demonstrated by comparing the behavior of the reinforced and the unreinforced containers. If water inflow is restricted by vent clogging or impermeability of the contents, it can be assumed that a structural failure of the container will occur. The concrete-shell fragments may be retained in place by mechanical interlocking alone. Reinforcement of the concrete by means of welded wire fabric is the most dependable and economical means of maintaining container integrity. A 44 by 44 wire fabric proved to be satisfactory; lighter wire fabrics were not investigated.

The required thickness of the concrete shell depends on several factors. Two-inch-thick reinforced-concrete interior shells appear to be suitable for vented container designs. It also appears to be important to use a very fluid concrete mix, which will flow into the unvented voids when vibrated, rather than higher strength mixes, which have inherently less slump and are more difficult to densify by vibration. The cracks that occur on drying a fluid mix also aid in venting the container. For a nonvented container a 4-in.-thick reinforced-concrete shell appears to be required for interior linings, with a thicker shell on the exterior. Whenever possible, fabrication practice should be such that voids are eliminated to the maximum extent practical; however, when voids are found, they should be filled with concrete. All impermeable type waste contents should be set in a concrete matrix or slurry, where the stiffness of the contents is not sufficient to prevent a local buckling failure.

Permeability and springback of waste materials seem to be the most important properties that determine container response to sea disposal. The benefits of compacting contents beyond a certain point, in order to provide stiffness and increase concrete-shell resistance to load, appeared to be insignificant. A top limit of compacting pressure of 100 psi is recommended, with a lower limit in the neighborhood of 5 to 10 psi.

Land Burial: Operating Experience

To assure adequate protection of public health and safety throughout the period of any potential hazard, AEC policy provides for permanent land burial on federal- or state-owned land of low-level packaged radioactive wastes generated in privately owned operations.[5,6]

The reported total of radioactive wastes that were buried[2] during the fiscal year 1961 in the

AEC burial grounds located at Savannah River, Idaho, Hanford, Oak Ridge, Los Alamos and Sandia, N. Mex., the Nevada Test Site, Weldon Spring, Mo., Fernald and Portsmouth, Ohio, and Paducah, Ky., was 3,309,000 cu ft. The Oak Ridge and Idaho burial sites, which were designated in 1959 as interim locations for use by licensees in disposing of suitably packaged low-level solid radioactive waste, reported a total of 74,400 cu ft of such wastes buried for licensees under the interim burial program and 20,600 cu ft of waste buried for other government agencies. The remainder of the 3,309,000 cu ft was generated by Commission and contractor activities.

A status report[7] on solid-waste disposal at ORNL has been issued. This study defines more specifically the geological and hydrological conditions that exist in Burial Ground 4, now abandoned, and describes the movement of radionuclides in the area and the amount of activity contributed by the burial ground to nearby White Oak Creek.

Burial Ground 4 is located ½ mile southwest of the ORNL plant site. The site is underlain by the Conasauga shale of Cambrian age. The area was opened in February 1951 and closed to routine burial operations in July 1959. It encompasses an area of about 23 acres, 1 acre of which remains available for burial. The burial rate during its 8.5 years of operation was approximately 2.5 acres per year.

The routine burial procedure consisted of burying the contaminated waste in trenches. In the case of trenches known to contain alpha-contaminated wastes, approximately 18 in. of concrete was poured over the filled hole. About fifty 15-ft-deep auger holes were used to dispose of small packages of higher level waste. Burial was limited to higher elevations within the burial ground during the wet periods, and the low topography was utilized during the dry summer months. Little information is available concerning the types, concentrations, and quantities of radionuclides disposed of at the site.

Activity has been detected in water samples from wells located within the burial ground. Most of the contaminated wells are located in areas of low topography where ground water contact with the waste is greatest. Many seeps are believed to emerge from the downslope end of covered trenches. Soluble waste material is also transported by ground water through the weathered soil to points of discharge in or near surface streams. Identifiable contaminants from wells, seeps, and streams within the area include Zr^{95}, Nb^{95}, Ru^{106}, Cs^{137}, Co^{60}, Sr^{90}, Po^{210}, Pu^{239}, Pu^{240}, and the rare earths.

Although radionuclides have been detected in wells, seeps, and streams in Burial Ground 4, the amount of activity contributed to White Oak Creek during the sampling period was so small in comparison to that already present that it could not be detected.

Treatment of Liquid Wastes by Separation of Specific Isotopes

Foam Separation

Foam separation[3,6] is being studied in a joint research project by Radiation Applications, Inc., and ORNL. It is being applied to the removal of strontium, cesium, or other radioactive elements from dilute low- or intermediate-level activities in ORNL wastes. ORNL is undertaking an engineering development program employing a 6-in.-ID countercurrent foam-separation column system that is based on the chemical systems and conditions specified by Radiation Applications, Inc., and ORNL.[8]

These laboratory and engineering process studies will show whether the chemical effects or the equipment scaleup are the principal problems involved in the application of foam separation to ORNL waste decontamination. If uncertain chemical effects remain, the 6-in.-ID column system could be altered slightly to permit semiremote operation using actual plant waste solutions. If equipment scaleup problems appear to be of major importance, a second scaleup to 24- or 36-in.-diameter colums might be desirable.

The foam-separation column is to be operated with countercurrent contacting of liquid and foam. The foam is generated in a pool of liquid at the bottom of the column by admitting gas through small nozzles or porous plates. The feed liquid is introduced in the middle of the column. Wash and/or reflux liquid is introduced near the top of the column. The foam is

condensed to give a liquid product stream and a reflux liquid if reflux is used. The foam breaker or condenser may be mechanical, thermal, or chemical in principle.

Three approaches are under consideration at ORNL in the application of foam-separation processes to the decontamination of low-level-activity wastes:[9] (1) removal of calcium, strontium, and cesium by foaming; (2) complexing of calcium by ethylene diamine tetraacetic acid (EDTA), or other agents, thereby holding calcium in solution while strontium and cesium are removed by foaming; and (3) partial precipitation of calcium and strontium by addition of sodium carbonate, sodium hydroxide, or sodium phosphate, followed by the removal of the solids by flotation and then the soluble cations by foaming. Cesium would be removed by adding finely divided clay, which strongly sorbs cesium, or by ferrocyanide, which forms a solid with cesium during the flotation phase.

Engineering studies of the 6-in.-ID column were started using isotopic exchange between Sr^{89} tracer and inactive strontium. Dodecyl benzene sulfonate (DBS) in $10^{-3}M$ sodium hydroxide was used as the surfactant complexing agent and foaming agent. Surfactant material balances from analyses by ultraviolet absorption were excellent, but gross β material balances were only 60 to 70 per cent. Based on the liquid phase, and considering the bottom of the column as one theoretical stage, 3.2 to 4.3 transfer units were obtained for 18 in. of countercurrent foam-liquid contact. These values are uncertain due to the poor tracer balance and a nonoptimum flow ratio resulting in pinching of the operating and equilibrium line.

In experiments with ORNL tap water containing added tracer strontium and sodium hydroxide, the resulting calcium-strontium precipitate was removed by filtration instead of by flotation.[9] The soluble strontium tracer was removed by foaming with DBS as the surfactant. In two tests with tap water made 5 and $10 \times 10^{-3}M$ in sodium hydroxide, approximately 90 per cent of the strontium and calcium precipitated. To each of the resulting filtrates, 62 mg of DBS per liter was added and the strontium distribution coefficient determined in a single-stage foam column. The strontium distribution coefficients were large enough to suggest that ORNL low-level-activity waste could be decontaminated from strontium in a countercurrent foam column after removal of most of the calcium.

Ion Exchange

ORNL has completed the construction of a 10 gal/min scavenging ion-exchange process pilot plant to study the decontamination of large volumes of low-activity contaminated wastes.[10,11] In this process the waste solution is adjusted to approximately *p*H 12 with sodium hydroxide, clarified, and passed through a bed of phenolic cation-exchange resin.

Following three demonstration runs with ORNL tap water, a 72-hr continuous run was made in which a total of some 45,000 gal of ORNL process waste, representing about 1600 bed volumes, was treated.[11] The major contaminants, strontium and cesium, were removed from the feed by factors of 3000 and 290, respectively. Analysis of plant effluent samples indicated 0.9 and 0.009 per cent of current MPC_w (maximum permissible concentration in water) values for Sr^{90} and Cs^{137} for a 168-hr week.

Holcomb and Roberts at ORNL have summarized the laboratory results of investigation on the use of the weakly acidic carboxylic-phenolic ion-exchange resin[12] (Duolite CS-100) instead of the phenolic-sulfonic resins originally proposed for the scavenging ion-exchange process.[10] The weakly acidic carboxylic-phenolic resin was shown to be as effective as the sulfonic-phenolic resin in the loading cycle and could be regenerated with $0.5M$ nitric acid instead of the $5M$ hydrochloric acid required for the phenolic-sulfonic resin. A disadvantage of this resin is its present noncommercial status. It is available on special order at about $50 per cubic foot. It is not an "experimental" resin, however, since it was formerly made commercially in large quantities.

At the ICPP the removal of strontium from acidic aluminum nitrate type waste solutions by adsorption on Amberlite 200 cation-exchange resin is being studied as a part of their long-range waste-treatment program.[6,13] Recent laboratory results indicate that salt cations at $1M$ concentration interfered seriously with the removal of strontium. For example, increasing the concentration of aluminum in solution from $0.1M$ to $1M$ decreased the amount of strontium adsorbed on a fixed-bed column of the resin from about 126 to 2 column volumes. Com-

plexing agents did not increase strontium removal; apparently the complexing agents function effectively only in a less acidic system. Conversion of the aluminum nitrate to basic aluminum nitrate of the approximate composition $Al(OH)(NO_3)_2$ also did not improve the strontium removal.

The laboratory data indicate that strontium can be removed from relatively acidic solutions without causing physical breakdown of the resin. However, the effectiveness of the ion-exchange process for removing strontium from an aluminum nitrate–nitric acid process waste will be highly dependent on the aluminum concentration. The concentration of aluminum nitrate in ICPP stored wastes, for example, is probably too high for removal of the strontium by ion exchange in Amberlite 200 resin without a pretreatment to reduce the concentration of aluminum.

Hanford is exploring the application of various natural minerals, synthetic inorganic zeolites, and organic resins in their over-all waste-fixation process.[1,14,15]

Duolite C-3 (a sulfonated phenol resin) was investigated for removing Cs^{137} from high-level-activity neutralized Purex supernatant waste. This is a high-sodium-content waste, and the major radioactive isotope is Cs^{137} (very little Sr^{90} is present). The selectivity of Duolite C-3 phenolic cation-exchange resin for cesium is known to increase[14,15] at high *p*H. Experiments have shown that the buffer capacity of the waste affects resin capacity more than *p*H per se.[15] Column experiments with Cs^{137} in 2*N* sodium carbonate (*p*H 11.8) and 2*N* sodium sulfate brought to the same *p*H with 2*N* sodium hydroxide exhibited marked differences in breakthrough points. The 50 per cent breakthrough points for carbonate and sulfate solutions were 208 and 137 column volumes, respectively. In other experiments with solutions having a *p*H of 9.9, 50 per cent column breakthrough was reached after 6 column volumes.[14] When caustic was added to the solution to give 3.1*M* hydroxyl ion, the 50 per cent column breakthrough volume was increased to 190 column volumes.

Cesium-137 sorption for this resin was demonstrated to be dependent on total cesium concentration even in high-sodium systems where cesium is in the "trace" concentration range.[15] The 50 per cent Cs^{137} breakthrough points for synthetic wastes containing cesium concentrations of $3.2 \times 10^{-3}M$, $4 \times 10^{-4}M$, and $1 \times 10^{-5}M$ were 15, 22, and 50 column volumes, respectively. The influent sodium concentration of these solutions was about 9*M*, and therefore the sodium-to-cesium ratios were from 3×10^3 to 1×10^6. Thus it appears that some exchange sites on Duolite C-3 are highly selective for cesium but that the number of these sites is very low. These results explain why nearly 10 times the volume of coating-waste supernatant solution can be processed to 50 per cent Cs^{137} breakthrough as compared to neutralized Purex high-level-waste supernatant solution.

Laboratory studies were made of the elution of cesium from Duolite C-3 resin.[14,15] Ammonium sulfate and ammonium sulfate–sulfuric acid mixtures were very effective. They were, in fact, superior to sulfuric acid alone, requiring about 3 to 3.5 bed volumes to elute 98 per cent of the Cs^{137}. Sulfuric acid alone required 20 bed volumes (2*N*) and 10.3 bed volumes (5*N*) to elute 98 per cent of the Cs^{137}. The use of ammonium ion is advantageous if the eluate were to be calcined later, because the ammonium ion would not contribute to the volume of calcined product.

Duolite C-3 was used in two runs made in the Hanford high-level cell to study the removal of Cs^{137} from actual neutralized Purex high-level-waste supernatant solutions.[14,15] In the first run, with a feed *p*H of 9.9, the early effluent showed a cesium decontamination factor[14] of 500. Cesium breakthrough reached 50 per cent after passage of 13 column volumes of solution and reached 75 per cent after passage of 15 column volumes. The bed was washed with water and then with 3.6 column volumes of 0.25*M* nitric acid. These washings removed about 4 per cent of the Cs^{137} and most of the sodium from the bed. The remaining Cs^{137} was then eluted with 20 column volumes of 1*M* nitric acid, giving 96 per cent recovery. Gassing of the column was observed and flow through the bed was blocked when, following elution with 1*M* nitric acid, wash water was started through the bed. The nitric acid is believed to have attacked the resin bed, thereby causing the gassing.[15]

In the second run the column influent was adjusted to 2*M* sodium hydroxide. The 50 per

cent Cs^{137} breakthrough occurred at 24 column volumes as compared to 13 column volumes when no sodium hydroxide was added. The rather low Cs^{137} capacity was due to the $10^{-3}M$ cesium concentration in the waste. Elution of the Cs^{137} was accomplished with $1M$ sulfuric acid. The concentration of Cs^{137} in the eluate increased to five times the waste influent level by the second column volume and then slowly decreased. Elution was essentially complete at 18 column volumes. The sulfuric acid did not attack the resin as did the nitric acid in the previous run.

In the Micro Pilot Plant, four extended-run adsorption experiments were made to investigate the treatment of Purex tank-farm condensate.[1,16,17] Experimental data have indicated that a more optimum decontamination of this type of waste can be achieved if the waste is passed through a sulfonated polystyrene cation resin column in series with a clinoptilolite column. In the Micro Pilot Plant runs, the waste is pretreated to remove organic and ammonia impurities by steam stripping, is passed through a bed of activated carbon to effect further reduction of the organic in the stripper bottoms, and is then passed through the cation-exchange (Amberlite IR-120) and clinoptilolite (particle size 0.5 to 0.9 mm) columns (operated either separately or in series combination). Both types of columns were operated in the hydrogen form.

The steam stripper has been operated for nearly 3000 hr, satisfactorily removing greater than 97 per cent of the ammonia and organic impurities from the condensate waste.[14] These impurities chemically interfere with ion-exchange reactions and physically foul the beds. The condensed overheads are from 4 to 7 vol.% of the feed and consist of two phases. In the three runs when the columns were not operated in series, the gross beta decontamination factors for the two cation-exchange bed runs ranged from 50 to 100 and 15 to 30 (no *p*H adjustment in the feed stream), and for the one clinoptilolite run the factors ranged from 10 to 30 (*p*H of feed stream adjusted to 3 with nitric acid before passage through the activated carbon).[14] Most of the gross beta activity in the effluent is due to Ru^{106}, which is not effectively removed by any of the materials tested to date. In the run where the columns were operated in series, the efficiency of these materials for removing strontium and cesium varied with the *p*H, the optimum *p*H being[15] about 4. Strontium was primarily removed by the resin, and cesium was primarily removed by the clinoptilolite.

Mercury-Cathode Electrolysis

An electrolytic method for the removal of fuel alloy metal ions from aqueous stainless-steel process wastes or dissolver solutions is being studied on a laboratory scale at the ICPP.[6,18–20] This method involves separation of the alloy metal ions, iron, nickel, and chromium, from the fission products and other waste constituents by mercury-cathode electrolysis. The metal alloy ions are transferred to a pool of mercury, and the fission products remain in the aqueous waste. The slightly contaminated alloy metals are then separated from the mercury and stored in low-cost containers or pits without cooling. The remaining acidic solution of fission products can be concentrated for storage as an aqueous solution or converted to a solid for final disposal.

Recent investigations were made to determine the rate of electrolysis of the alloy metal ions from a synthetic stainless-steel waste and to estimate the loading capacity of the stainless-steel alloy metals in the mercury.[18–20]

The laboratory data indicate that iron, nickel, and chromium can be removed from a dilute sulfuric acid solution without appreciable contamination by fission products. The calculated quantity of electricity required to effect this removal is approximately 85 amp-hr per liter of waste, with a current efficiency of about 12 per cent. The loading capacity of the mercury for the alloy metals appeared to be about 2 wt.%, although it may be somewhat higher with a more efficient cell design. Calculations based on the current requirements indicate that 5.3 m^2 of mercury are required to remove the stainless-steel metal ions from 3740 liters of a "typical" stainless-steel waste containing $0.1M$ stainless-steel metal ions in 24 hr. This quantity of waste results from the chemical processing of 10 kg of uranium. Similar calculations based on the estimated mercury-loading capacity indicate that 1200 kg of mercury are required to remove the stainless-steel ions in a single pass.

Conversion of High-Level-Activity Liquid Wastes to Solids

In-Tank Solidification

At Hanford the development emphasis for production treatment of its Purex-plant high-level wastes has changed from bulk calcination to extraction and separate storage of the relatively long-lived heat-producing radionuclides (e.g., cesium, strontium, and rare earths) and in-tank solidification and storage of the bulk salts after adequate decay of the shorter-lived radionuclides.[1,15] This approach is being investigated because it offers over-all advantages at Hanford as an integrated approach to waste management and fission-product recovery.

Submerged combustion or the direct contact of hot gases with a solution to be heated and concentrated is considered as a potential, simple means of concentration of wastes in large underground storage tanks. Preliminary work was aimed at entrainment control. Extensive investigation by Rey[21,22] has resulted in a system for entrainment control of the off-gas stream from submerged combustion concentrators which removes many of the drawbacks of this efficient method of reducing liquid volumes. Studies resulted in establishment of performance characteristics of semiworks-scale submerged combustion units using water and various salt solutions.

Correlated test data established that various effects could be disregarded in the over-all deentrainment or could be circumvented by equipment design. For example, the boilup rate in a tank of fixed diameter establishes the superficial vapor velocity in the vapor space of the evaporator. Entrained droplets with terminal settling velocities equal to or less than the established vapor velocity are carried along with the vapor toward the condenser. In the test-equipment investigation, this velocity was less than 1 ft/sec, whereas commercially designed evaporators operate at vapor velocities of greater than 2 ft/sec. Less than a twofold decrease in entrainment was measured when the boilup rate was decreased by one-half, indicating that the effect of boilup rate on entrainment is not of major importance. Foaming was visually observed to have practically no effect on entrainment, but rather the addition of antifoam agents actually increased the deentrainment problem since the addition of such agents tends to reduce the surface tension of the solution.

The major variable affecting entrainment was the gas temperature entering the solution. As shown in Fig. IV-2, this effect is quite pronounced. Experimental work determined that several methods could be employed to arrive at the optimum entrance gas temperature of about 750°F. One method transfers a portion of the sensible heat of the gas through the walls of the combustion tube to the bulk of the solution prior to entry of the gases into the solution, in effect cooling the combustion products as well as preheating the solution.

Additional semiworks-scale tests employing a propane burner rated nominally at 1 million Btu/hr were aimed at resolving questions of solids-deposition pattern, hydration phenomena, and process-control techniques, as well as the volume reduction necessary for immobilization of synthetic waste solutions. These tests were conducted in 5000-gal tanks. The burner was elevated above the solution level, thus providing a greater length of combustion tube to reduce the entrance gas temperature to approximately

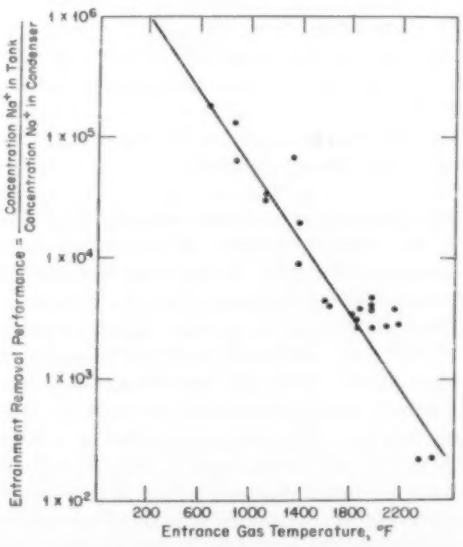

Fig. IV-2 Effect of entrance gas temperature on entrainment by hot gas sparging.[15]

750°F before dispersing it into the solution. The bottom portion of the combustion tube was also provided with a crow's-foot distributor to eliminate complete blocking in the event that the normal gas distributor holes became plugged during operation. Hot gases are discharged into an airlift circulator tube surrounding the combustion tube. Thus the concentrating material is vigorously circulated.

The following results were obtained in a series of runs:

1. The entrance gas temperature could be maintained below 750°F without the addition of excess air because the longer combustion tube permitted dissipation of heat through the tube wall to the solution.
2. The airlift circulator ceases to function when the liquid submergence becomes less than 20 per cent of the total lift.
3. Scaling of the airlift circulator and combustion tubes does not occur where these components are wetted by the circulated solution.
4. Solids deposited evenly across the bottom of the 5000-gal tank, but scaleup (to about 75 ft in diameter) was not studied.
5. The presence of chemically degraded Purex solvent (30 per cent tri-*n*-butyl phosphate in hydrocarbon diluent) does not result in foaming problems since the organic readily distills away.
6. Evaporation of a synthetic Purex alkaline waste supernatant solution to 41.5 per cent of the original volume results in essentially complete solidification after subsequent cooling to 40°F.
7. There was no tendency for the distribution ports to plug during operation.

Laboratory studies were conducted to determine the characteristics of the solids which would be produced by in-tank solidification of radioactive waste solutions by sparging with a hot gas. Solutions simulating Purex coating-removal waste, supernatant liquid from stored alkaline Purex 1WW, and combinations of these two wastes were evaporated to dryness while being sparged with either air only or a 50-50 mixture of air and carbon dioxide. Solids produced during sparging with air only are deliquescent on exposure to air at laboratory temperatures and humidity. Those produced with carbon dioxide in the sparge gas appear stable to laboratory air. When the air–carbon dioxide mixture was used for sparging, solids tended to cake on and plug the sparge tube.

Spray Calcination

Hanford is studying a calcination process for the treatment of Purex high-level-activity aqueous wastes which combines two types of calciners: the radiant-heat spray and pot calciners (references 1, 14, 15, and 23). Equipment is being fabricated and assembled for small-scale studies with actual Purex wastes in calciners to be located in the High-Level Radiochemistry Facility.[14,15] Figure IV-3 is an isometric sketch of the layout of the radiant-heat spray calciner, melt pot, and their associated equipment. The system is designed to process full-level-activity Purex 1WW at a feed rate of 1 gal/hr until the 0.8-gal melt pot is filled. Thus, if a 10-fold volume reduction is achieved, an 8-hr-long run will be possible, equivalent to processing the waste from approximately 0.2 ton of irradiated uranium.

The off-gas train consists of a sintered stainless filter, an all-glass condenser, a Raschig-ring-packed scrubber, a second scrubber, a silica-gel bed, and two AEC filters. The second scrubber is a bubbler that will be replaced with an electrostatic bubble scrubber. It has a preionizing stage to allow the particles to achieve a greater charge before impinging on the scrubbing liquid. The design gas flow is 2 cfm.

A prototype spray-calciner unit is also being constructed for large-scale studies with nonradioactive solutions.[14,15,23] It is being designed to operate either as a radiant-heat spray calciner or as a direct gas-heated flame denitrator. The pilot plant will consist of an 18-in.-diameter 10-ft-long Inconel X tube inside a resistance-heated tube furnace. It will have a nominal capacity of 20 gal of simulated waste per hour. The feed solution and the fuel, in the case of gas heat, are introduced at the top of the reactor. The dried solids and reaction gases flow concurrently through the reactor to a battery of gas-solids separators.

Fluid-Bed Calcination

The ICPP is continuing its development of the fluidized-bed calcination of high-level-activity aluminum nitrate waste solutions, which are converted to solid alumina form.[1,13] A 60 gal/hr

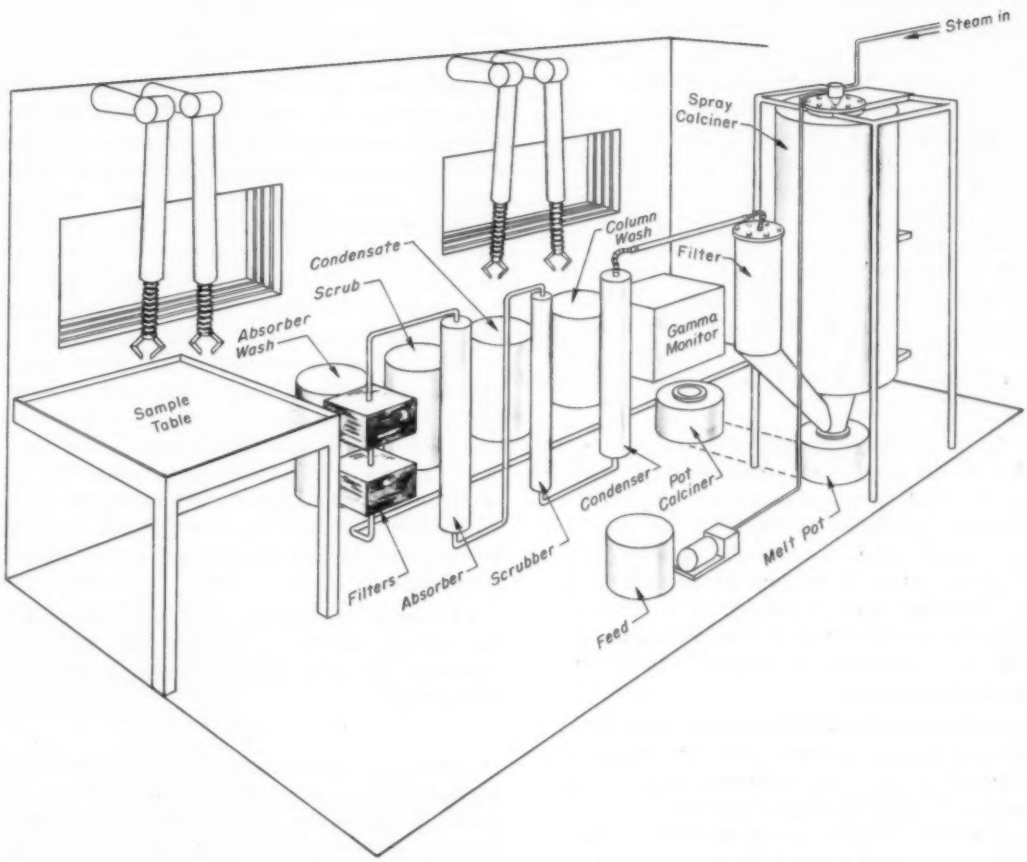

Fig. IV-3 Hanford waste-processing high-level cell facility.[23]

fluidized-bed calciner, the Demonstrational Waste Calcining Facility, which is designed to demonstrate the feasibility of this process, is undergoing testing.

Pilot-plant studies have continued in the 2-ft-square calciner with production, for the first time over a prolonged period of continuous operation, of alpha-alumina-free product from a feed containing substantial sodium.[13] Sodium has been considered a promoter of alpha-alumina growth, and no explanation of its lack of effect in this case has been developed. Intraparticle porosities ranging from 0.4 to 0.60 were obtained, emphasizing the effect of bed temperature (250 to 550°C), primarily, and the feed concentration (0.8*M* to 1.95*M* aluminum nitrate), secondarily, on this property. Low temperatures and low feed concentrations favor low product porosity. The starting bed material is sand.

The calcination of synthetic aluminum nitrate–nitric acid process waste solutions in a fluid-bed calciner has produced both amorphous alumina and crystalline alumina species, such as alpha and gamma alumina, depending on the composition of the waste and the calcination conditions.[13] Laboratory work was continued in an attempt to find calcination conditions that would minimize the amount of alpha-alumina formation. The alpha-alumina form (crystalline) undergoes severe attrition in a fluid-bed calciner and results in excessive loading of alumina "fines" in the off-gas.

Laboratory data have indicated that the conditions under which the aluminum nitrate was converted to amorphous aluminum oxide had a definite influence on the rate of conversion of amorphous alumina to alpha alumina in a calciner atmosphere. For example, alumina pre-

pared in the laboratory by various methods, including thermal decomposition of aluminum nitrate in air and precipitation of hydrous aluminum oxide by ammonium hydroxide or sodium hydroxide, consistently failed to form alpha alumina when heated in a laboratory test unit. However, samples of amorphous alumina from two different runs in the cold pilot-plant calciner consistently formed about 65 and 10 per cent alpha alumina, respectively, when heated in a laboratory test unit. Attempts at correlation of the marked difference in "alpha-forming ability" of alumina prepared in different runs in the fluid-bed calciner with specific calciner variables have not been successful.

It was previously reported that sodium was needed in the amorphous alumina to cause the formation of alpha alumina in the relatively low calcination temperature range[1,13] of 400 to 500°C. Recent laboratory results indicated that the rate of change from amorphous alumina to alpha alumina during heating in a calciner atmosphere was different if solid sodium nitrate instead of a solution of sodium nitrate was added to the alumina.

Contacting the amorphous alumina with water or sodium nitrate solution prior to heating in the laboratory test unit definitely inhibited the formation of alpha alumina. This was true even though the 1*M* sodium nitrate solution actually resulted in a slight increase in the total sodium content. For example, contacting a sample, which contained 2.3 wt.% sodium, with water or sodium nitrate solution reduced the amount of alpha alumina formed during heating to about one-fourth of the value obtained without any pretreatment.

Adding solid sodium nitrate to a sample that contained 1.7 per cent sodium and to a sample that did not contain sodium increased the amount of alpha alumina formed during heating by a factor of 3 to 4. Thus a positive effect of adding sodium is evident not only on a sample that was prepared originally without sodium but also on a sample that appeared to contain adequate sodium to effect the conversion to alpha alumina. For reasons not yet established, the sodium that was already in the sample was not effective in promoting the conversion to alpha alumina.

Sodium oxalate, potassium nitrate, and cesium nitrate also promoted the growth of alpha alumina, although to a lesser degree than sodium nitrate. Sodium sulfate was not effective in promoting growth of alpha alumina in the one experiment where it was used.

Laboratory data indicate that the short residence time in the calciner and the removal of sodium from the calciner feed are the two most effective means of reducing the amount of alpha-alumina formation in a fluid-bed calciner. Neither of these approaches is very practicable for the calcination of stored process wastes in the ICPP fluid-bed calciner, although a better definition of the rate of formation of alpha alumina as a function of sodium concentration in the feed may show that some of the stored wastes are within the necessary limits. An attempt is currently being made to define these limits by preparing alumina under a variety of conditions in a small 2-in.-diameter laboratory calciner. An investigation will be made of the possibility of inhibiting the growth of alpha alumina by the use of additives in the calciner feed solution.

Additional laboratory data have shown that the nitrate content of amorphous alumina is inversely related to the bed temperature during calcination.

Laboratory investigations were continued on a precipitation-calcination method for the treatment of zirconium process wastes containing fluoride (STR types).[1,11] The precipitation step converts the fluoride to a compound or compounds that will retain the fluoride in the calcined product during calcination. Previous experiments showed that calcium oxide added to a synthetic STR type waste precipitated the fluoride, if allowed to remain in contact with the solution for several hours. Precipitation conditions were found which gave the most rapid precipitation (<5 min) of the fluoride. Precipitation of the zirconium, fluoride, and aluminum was achieved by addition of calcium oxide (CaO/F ratio = 1.5) as a slurry at 60°C. The rapidity and completeness of the reaction indicate that a continuous precipitation step just prior to calcination might be feasible.

Pot Calcination

ORNL is investigating the permanent disposal of high-activity wastes by conversion of the liquids to solids by high-temperature pot calcination or fixation in the final storage container

(pot) itself and storage in a permanently dry environment such as a salt mine.[1,11] This is considered an extremely safe method since complete control of radioactivity can be ensured within present technology during treatment, shipping, and storage. This is being studied on both an engineering and a laboratory scale with synthetic Purex, Darex, and TBP-25 wastes containing millicurie amounts of ruthenium. The data and flow sheets developed from these investigations are being used for the design of a pilot plant to be built at ICPP.[10]

Ten waste-calcination runs (six with TBP-25 and four with Purex waste) were completed in the engineering-scale, 8-in.-diameter by 90-in.-high, stainless-steel calcination pots (Table IV-1).[11,24] Six runs were made with a continuous evaporator, closely coupled to the pot, and four with feed prepared in a batch evaporator. Control of both systems was good except for feed-line plugging at high concentrations.[11] With prolonged feeding time, average feed rates decreased, but the bulk density of the calcined solids increased. An economic stopping point may be determined by balancing operating time against basic fixed cost. Ruthenium volatilization was negligible. In five tests in which stable ruthenium was added to the feed, ruthenium in the evaporator condensate was below analytical detection except during minor upsets at the start of each test.

The phosphate concentration in the Hanford Purex 1WW is of the order of 0.01*M* and as much as 120 ppm of TBP and organic diluent in the Purex tank-farm condensates. The addition of 1 ml of MBP (monobutyl phosphate) and DBP (dibutyl phosphate) per liter of waste to the evaporation-calcination feed caused severe foaming and entrainment, resulting in lower average feed rates (Table IV-1). In laboratory-scale tests, antifoam additives broke the foam satisfactorily at or near the solution boiling temperature but volatilized as the solution was concentrated to about one-third of its original volume.

Severe foaming may not be encountered in calcination of ICPP TBP-25 waste. No appreciable foaming of this waste was noted when an active sample was evaporated to dryness, although simulated TBP-25 waste with added DBP produced considerable amounts of foam.

In another series of 11 tests with simulated Darex and TBP-25 wastes and TBP-25 wastes

Table IV-1 ENGINEERING-SCALE POT-CALCINATION TEST CONDITIONS AND RESULTS[11]

Feed composition							
Purex				TBP-25			
Fe^{3+}	0.5*M*	Al^{3+}	0.1*M*	Al^{3+}	1.7*M*	Na^{+}	0.05*M*
SO_4^{2-}	1.0*M*	Na^{+}	0.6*M*	Hg^{2+}	0.02*M*	NO_3^{-}	5.8*M*
Cr^{3+}	0.01*M*	NO_3^{-}	6.1*M*	Fe^{3+}	0.008*M*	H^{+}	1.2*M*
Ni^{2+}	0.01*M*	H^{+}	5.6*M*				

Run no.	Feed type	System*	Concentration factor	Water-to-feed ratio, liters/liter	Off-gas to feed ratio, cu ft/liter	Nitrate in calcined solids, wt.%	Bulk density of calcined solids, g/cm³	System feed rate (av.), liters/hr
43†	Purex	Continuous	1.3–2.2	Leak	Leak	0.008–0.9	1.28	50.0
44†	Purex	Continuous	1.3–3.8	7.8	2.02	0.06–0.14	1.14	40.9
45	Purex	Batch	0.98–1.35	3.9	2.20	0.01–4.7	1.17	25.2
46	Purex	Batch	0.98–1.27	4.1	3.50	0.01–3.7	1.55	25.8
47	TBP-25	Continuous	1.2–2.3	3.4	1.90	0.36–6.0	0.57	30.6
48	TBP-25	Continuous	0.93–1.6	2.8	3.50	0.10–6.0	0.77	15.0
49	TBP-25	Continuous	0.8–1.25	2.6	1.90	0.36–6.0	0.83	17.6
50‡	TBP-25	Continuous	0.8–1.47	2.4	2.40	0.08–4.1	0.52	11.5
51‡	TBP-25	Batch	1.18–1.38	2.5	3.20	0.08–6.0	0.59	7.0
52‡	TBP-25	Batch	1.09–1.44	2.3	2.40	0.06–0.18	0.44	9.8

*Batch-system capacity is 600 liters; continuous-system capacity is 25 liters.
†Stable ruthenium added to feed.
‡Monobutyl phosphate and dibutyl phosphate added to feed.

containing organic residues, average over-all evaporation-calcination rates for the full-scale (96 in. high by 8 in. in diameter) pot calciner decreased with increased filling (evaporation) time.[25] This is attributed to the higher bulk densities and consequently higher thermal conductivities in the final product. Both batch and continuous flow sheets were demonstrated along with satisfactory control of the continuous evaporator. Filling rates averaged 8.6 to 19.4 liters/hr, depending on feed type, concentration, and filling period, with final solid-product bulk densities ranging from 0.61 to 1.42 g/cm^3.

A lead phosphate glass was produced by semicontinuous evaporation, calcination, and heating to 1000°C of a simulated TBP-25 waste solution to which 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO per liter had been added.[11] The product, which had a density of ~2.9 g/cm^3 (1 volume of glass representing 8 volumes of waste), compared favorably with the product of a batch experiment, which had a density of 2.84 g/cm^3 (1 volume of glass representing 8.1 volumes of waste). About 90 per cent of the mercury and 24 per cent of the ruthenium were volatilized, the latter believed due to equipment malfunction. One approach under consideration to handle the mercury that volatilizes in the TBP-25 calcination process is to install a mercury trap in the calciner off-gas line operating at a temperature low enough to condense or absorb the mercury in whatever form it may be but high enough to keep the nitric acid going through the mercury trap as a vapor.[26] This mercury trap could be removed from the process when filled and disposed of as a separate item.

Cesium volatility probably will not be a problem in formation of a glass from waste containing sufficient acid oxides[11] such as phosphorus pentoxide (P_2O_5). In laboratory-scale experiments, simulated TBP process waste containing 0.1 μc of Cs^{137} tracer per milliliter was evaporated and calcined to 1000°C. As glass-forming and fluxing agents, 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO were added per liter of waste. The glass produced contained 26 wt.% waste oxides and had a density of 2.84 g/cm^3. The volatilization of cesium was <0.3 per cent. In similar tests, ruthenium was 60 to 0.7 per cent volatilized in the presence of 0 to 2 moles of phosphoric acid when the experiment was performed in a quartz pot versus 47 to 0.11 per cent in a stainless-steel pot.

The lead phosphate glass prepared above with Cs^{137} tracer was leached at rates that decreased from 2.1×10^{-6} to 2.5×10^{-7} g/(cm^2)(day) as measured at the end of the first and fifth weeks, respectively.[11] This corresponds to 4.9×10^{-4} and 5.5×10^{-5} of the original Cs^{137} leached in the first and fifth weeks, respectively. These results compare favorably with those obtained at Harwell with silicate-borate glasses containing approximately the same percentage of oxides from waste but are about one order of magnitude higher than the results at Chalk River with nepheline syenite–lime glasses containing about one-third this amount of waste oxides.

Godbee and Clark[27] at ORNL discuss, in a paper presented at the Spring Meeting of the American Chemical Society, Washington, March 1962, the use of phosphite and hypophosphite for controlling the volatility of ruthenium[1] in the evaporation and calcination of high-level-activity waste solutions. Phosphite and hypophosphite ions are reducing agents for fixing ruthenium in stable solid media and are oxidized to phosphate, which is a glass former. In this process the waste is fed into an evaporator as in the pot-calcination process. The evaporator bottoms then go to a hold tank, between the evaporator and the pot calciner, where phosphite and hypophosphite are added to control ruthenium volatility and to serve as a source of phosphate for forming glass. Other glass-forming additives are also added to the hold tank. The off-gas from the hold tank, mainly nitric oxide (NO) from the nitrate-phosphite-hypophosphite reaction, may be stored for subsequent use in controlling ruthenium volatility or oxidized to nitrogen dioxide with oxygen addition and absorbed in a scrubber downstream from the rectifier. The mixture from the hold tank then goes to a heated pot, where it is evaporated to dryness, calcined, and melted at 850 to 1050°C.

Ruthenium volatility from simulated Purex, TBP-25, and Darex waste solutions was studied during evaporation of the solutions, calcination of the dried solids, and incorporation of the calcined solids in melts with selected additives. The effect of phosphite (HPO_3^{2-}) and hypophosphite ($H_2PO_2^-$) on ruthenium volatility from these waste solutions was investigated both with and without the addition of glass-forming ingredients. All waste solutions studied contained 0.2

mg of stable ruthenium* per milliliter and 0.1 μc of Ru^{106} tracer per milliliter. Stable and radioactive ruthenium were added as the chlorides.

Relatively small concentrations of phosphite and/or hypophosphite were very effective in preventing volatilization of ruthenium from these waste solutions during evaporation. Ruthenium volatility was decreased to less than 0.1 per cent during high-temperature (~1000°C) calcination of Purex and TBP-25 wastes made approximately 2*M* in phosphite or hypophosphite. As little as 0.1 mole/liter lowered the ruthenium volatility during equilibrium distillation by factors that varied from 38 for Darex to 225 for TBP-25 waste solutions. The final products were insoluble glassy solids with densities of 2.4 to 2.8 g/ml and represented volume reductions of 5.5 to 8. These volume reductions are essentially the same as those obtained when the waste is calcined without additives. Since dense phosphate products with relatively low (850 to 1050°C) melting points can be made from both Purex and TBP-25 wastes, operation at these temperatures allows the use of stainless steel instead of ceramic containers.

In the pot-calcination process, the average processing rate decreases as the filling of the calcination vessel progresses. As indicated above, there must be an optimum filling point, when calcination vessel costs are balanced off against plant capital costs. Such an optimization based on expected pilot-plant costs would be of little value because the objectives (and hence the production rate and operating costs) of the pilot plant will be entirely different from those of a production plant.

Perona[28] at ORNL has calculated these optimum filling points based on the calcination of the wastes from the 15,000-Mw(e) nuclear economy being examined in the ORNL long-range studies for the economics of high-level-waste treatment and disposal.[1] The variables in his study were vessel diameter and waste composition (acidic or neutralized) for a plant processing Purex and Thorex wastes. Vessels were assumed to be 90 per cent filled in all cases, the 90 per cent point being chosen as a compromise between good processing rate and good vessel utilization. An algebraic expression was developed for cost as a function of the normalized radius of the central void space in a partially filled vessel. Minima of this expression were found for acidic and neutralized wastes in 6-, 12-, and 24-in.-diameter vessels.

Optimum fill volumes decreased as vessel diameter increased, varying for acidic wastes from 99.8 per cent for 6-in.-diameter vessels to 92.5 per cent for 24-in.-diameter vessels. Decreases in costs by using optimum fill volumes instead of the 90 per cent fill volume assumed for all cases in the long-range study were small, the largest being an 8 per cent decrease for neutralized wastes in 6-in.-diameter vessels.

ORNL has completed flow sheets for TBP-25 process waste for the ICPP Waste Calcination Pilot Plant (references 10, 11, 24, and 26). Darex and high-sulfate Purex flow sheets are being prepared. A total of eight will be made, one batch and one continuous for each of the TBP-25, Darex, high-sulfate Purex, and low-sulfate Purex processes. The TBP-25 waste flow sheet is receiving prime attention since its calcination will be tested first at Idaho.[24] The furnace will be designed to handle 6-, 8-, or 12-in.-diameter pots with an active length of 6 ft. Over-all pot length will be 7.5 to 8 ft. The process equipment sizes will be determined by the 12-in.-diameter pot size. Major equipment items and maximum flow rates and liquid volumes for the ICPP pilot plant are shown in Fig. IV-4.

Design of the test pieces and equipment is nearly complete for the mechanical development program for the radioactive pilot plant. This pilot plant will be tested in the Lockheed Nuclear Products Cell at Dawsonville, Ga.

Preliminary engineering flow sheets and cell layouts were prepared for radioactive cell studies of evaporation and calcination of actual high-activity wastes. Design of several vessels was completed, and fabrication was started. This equipment will be used primarily to study fission-product volatility during evaporation and calcination but will also provide solids that can be studied for radiation stability and analyzed for fission-product distribution. The proposed calciner pot dimensions are 4 in. in diameter by 24 in. high, and the maximum size of the

*This concentration is typical of ruthenium to be expected in a Purex waste solution for a low-burnup reactor and is about 10 times that to be expected in a typical TBP-25 waste.

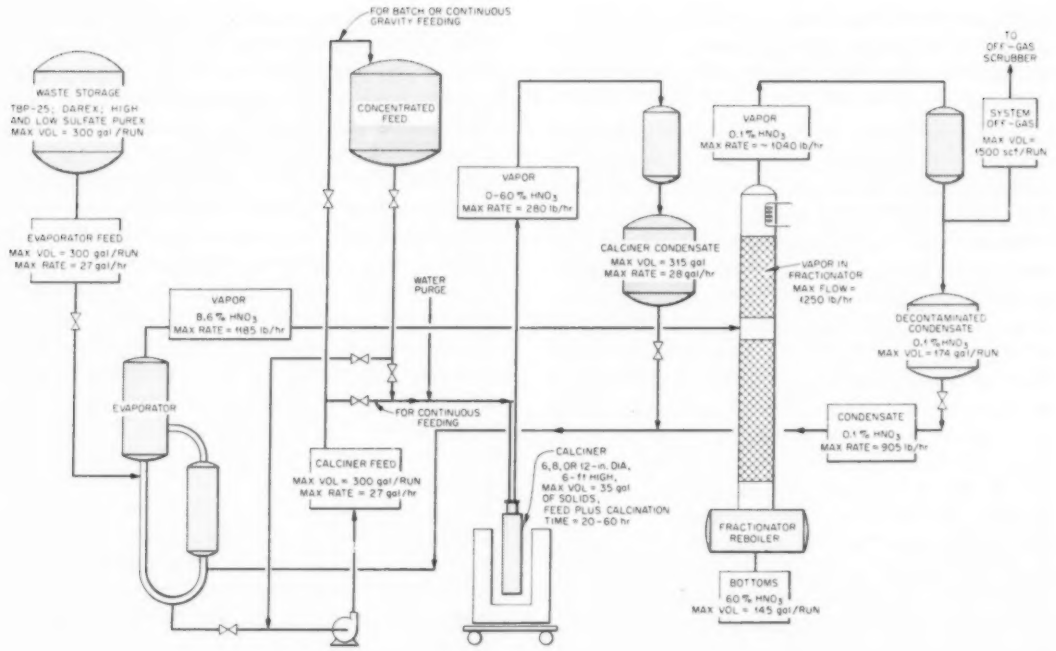

Fig. IV-4 ICPP pot-calcination pilot-plant flow sheet.[11]

feed batch, as determined by the capacity of the available intersite solution carrier, will be 5 gal.[24]

ORNL data[25] show that type 304 stainless steel should be a satisfactory material for waste calcination pots, with negligible corrosion in storage.[10] Corrosion was maximum during the period when the last of the acid and water were being driven off at 850 to 1000°C. Over-all corrosion in 24-hr evaporation-calcination of Purex and TBP-25 wastes was 0.26 to 0.34 mil at 900°C (8 to 10 mils/month). Of this, about 0.4 mil was attributable to air oxidation. When glass-making additives were present, rates were about 42 mils/month for a Purex borophosphate glass at 900°C. Release of SO_3 from the Purex caused aggressive intergranular attack (possibly catastrophic) at temperatures above 900°C, the critical temperature, depending on the melt composition.

Final Disposal

Seepage Pits

Although the seepage pits at ORNL are doing an effective job in the decontamination of the intermediate-level waste stream before it reaches the surface waterways of White Oak Creek and the Clinch River, ORNL is continuing to develop new methods of disposal which will provide greater control over the movement of the discharged wastes.[1,6] The use of a mineral-filled column looks very attractive. It would provide an efficient and inexpensive method for waste decontamination. The quality of the effluent could be accurately monitored and controlled, and the exact definition of the boundaries of the sorbed nuclides would be established.

In large-scale vermiculite column tests reported by Jacobs at ORNL,[29] four columns (2 in. in inside diameter and 10 ft in length) were tested for the removal of cesium and strontium from simulated ORNL intermediate-level waste. In general, the results indicate that the use of vermiculite-filled columns is feasible for cesium and strontium removal from this waste stream. The addition of potassium dihydrogen phosphate (KH_2PO_4) was found to be beneficial for removal of both cesium and strontium. Potassium, by initiating lattice collapse, improved cesium removal, and the presence of phosphate, in this highly basic solution, improved the removal of strontium. These studies

indicate that at least 5×10^5 gal of this waste stream could be decontaminated, with respect to cesium and strontium, by a column 10 ft high and 10 ft in diameter. The breakthrough curves are sufficiently sharp to indicate that the entire saturation capacity of the first column could be utilized if two columns were run in series and operated at a flow rate of approximately 0.5 gal/(sq ft)(min).

Most of the cationic fission products in the highly basic ORNL intermediate-level waste are retained in the seepage pits excavated in Conasauga shale by a combination of selective ion exchange and precipitation, thus reducing their rate of travel to a small fraction of that of the ground water. However, ruthenium moves through the ground nearly as rapidly as the ground water, although at some distances from the pits its concentration in the ground water is lower than predicted by simple dilution and decay, indicating some removal by the shale.[11] A study of ruthenium retention was undertaken because, in spite of the comparatively high permissible limits for Ru^{106}, its continued discharge to the environment constitutes a nuisance. Because of the chemical nature of ruthenium, a twofold approach was attempted: (1) replacement of ruthenium for other lattice ions as the surface of sulfide minerals, taking advantage of the insolubility of laurite (RuS_2); and (2) reduction of ruthenium to a positively charged species for subsequent sorption by natural cation exchangers.

Vermiculite and four sulfide minerals — pyrite (FeS_2), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), and stibnite (Sb_2S_3) — were investigated for adsorption of ruthenium. Ruthenium sorption from waste-pit seepage solution by both sulfide minerals and vermiculite was low; however, the more easily sorbed species would have been removed as the waste percolated through the ground to the seep. Strong reducing agents ($Na_2S_2O_4$) in alkaline media improved sorption if sufficient quantities were used, but the sulfide minerals did not reduce ruthenium to an easily sorbed form. Sorption on sulfide minerals from synthetic waste was appreciable when the ruthenium was in a suitable chemical form. Ruthenium removal from seep solution was optimum at *p*H 6 to 11, suggesting that continued removal of ruthenium in the ground results primarily from filtration of polymeric ruthenium dioxide.

Calcined Solids Storage in Salt Mines

ORNL is continuing its investigation on the technical feasibility of using salt mines for the storage of packaged calcined wastes.[1,6,11]

Previously reported studies on the effect of gamma radiation on the structural properties of rock salt showed that gamma dosages to 1×10^8 r produced negligible changes in creep rate and compressive strength.[6] However, dosages above this value may produce significant changes, i.e., decrease in compressive strength and slight decrease in creep rate. Since the salt in rooms containing radioactive waste will continue to be exposed to radiation for long periods of time, it is possible that the 1×10^8 r dose will be exceeded at the surface of the walls. A computer program was developed by the MIT Engineering Practice School to determine the gamma-radiation dose in the floor, walls, and ceiling of rooms in which packaged solid wastes are buried in the floor.[11] Results for 6-in.-diameter vessels containing two-year-cooled pot-calcined acid Purex waste, spaced at 5-ft centers, indicate that the total cumulative dose in salt at the center line between cans will be of the order of 3×10^6 rads. (The vessels were assumed to be buried 7 ft beneath the floor of a 15-ft-high 50-ft-wide very long room.) The results also indicate that the gamma dose in the ceiling is less than that in the floor and that the dose between pots is nearly constant across the room. The only sources that contribute significantly to the dose at a point are the two pots on either side of it. If cooling time before storage is increased from 2 to 14 years, the total gamma dose between pots is reduced more than half.

The amounts of floor area to be mined for the storage of calcined solid wastes in rooms in salt deposits were calculated for storage of Purex and Thorex wastes from a 15,000-Mw(e) [70,000 Mw(t)] nuclear economy.[11] Criteria for storage were that the calcined solids in cylindrical vessels must not exceed 1650°F (the maximum calcination temperature) and that the salt surface must not exceed 400°F. Previous infinite slab heat calculations assumed that all the wastes were generated at the same time. The actual case will more nearly approximate

a continuous generation of wastes, and the slab calculations were therefore redone with the assumption of a continuous accumulation of wastes with optimum dead storage time in tanks.[10]

The new slab calculations affect the curves previously reported[1] (Fig. IV-4) over the region from 0.33 to 8 years of age of waste at burial, shifting them upward for a maximum of about 20 per cent for wastes of about one year. The net result is that slightly more mine area is required to store wastes aged less than 8 years, e.g., 36 acres/year (gross) for one-year-old wastes rather than the 31 acres indicated.

For storage in 6-in.-diameter vessels, the minimum decay time from reactor discharge to storage in salt for acidic Purex waste is about 1.1 years but reacidified Purex, acidic Thorex, reacidified Thorex, and acidic Thorex glass could be stored immediately after processing (120 days after reactor discharge). For storage in 24-in.-diameter vessels, minimum decay times varied from 0.63 year for reacidified Thorex to 8.3 years for acidic Purex waste. Mined space requirements for calcined solids stored above the floor varied from 14.8 acres/year with a 0.33-year decay time to 2.25 acres/year with a 30-year decay time, a factor of 2.3 less than for storage of liquid wastes. The net yearly amount of mine space required for various fuel-processing wastes if buried at the minimum age varies from 1.26 acres/year for acidic Thorex in 24-in.-diameter vessels to 11.45 for reacidified Purex waste filled twice in 6-in.-diameter vessels.

Space requirements to dissipate the fission-product heat in the waste from a 56,000-Mw(t) nuclear power economy were also calculated for cylinders of calcined waste buried vertically in the floors of rooms in salt media.[25] Net area requirements calculated for burial of Purex wastes in acidic and reacidified forms in 6-, 12-, and 24-in.-diameter vessels range from 20 acres/year after aging 0.65 year to about 2 acres/year after aging 30 years. Corresponding results for Thorex wastes are 10 and 0.7 acres/year. Calculations were also made for an acidic Thorex glass in 6-in.-diameter vessels. The primary effects of the form of the waste (acidified, reacidified, glass) and vessel diameter are to limit the minimum burial age, although area requirements may be affected by factors of 2 to 3 by waste form and vessel size near the minimum burial ages.

Disposal in Deep Impermeable Formations

The Savannah River Plant has undertaken to investigate the feasibility of storing long-cooled fuel-processing wastes in underground caverns mined out of the impermeable bedrock 1200 ft or more beneath the plant.[2,3] Preliminary estimates are that costs would be comparable to those of present tank construction for uncooled wastes.

In January 1961 an exploratory drilling program was initiated at the Savannah River Plant in cooperation with the U. S. Army Corps of Engineers and the Geological Survey. Approximately 10 holes were to be drilled into the bedrock to obtain and analyze core samples for physical, chemical, and radiological compatibility with the wastes. The first hole, completed to 1900 ft, of which 1000 ft was in bedrock, found the upper portion of the bedrock broken but lower levels more intact. Physical appearance of the core samples was encouraging, and three more exploratory holes are being drilled.

Hydrologic studies will determine the occurrence and movement of ground water in the overburden of the bedrock to assure that water supplies will not be jeopardized. Other studies will define heat-generation rates of the wastes, age of waste to be stored, the potential radiation damage, and the physical form of waste considered best for storage. A schematic drawing of the proposed mine caverns is shown in Fig. IV-5.

Disposal in Abnormal-Pressure Reservoirs

Katz at the University of Michigan discusses the possibility of using this type of leaktight reservoir, found along the Gulf Coast, for storing radioactive liquid wastes.[30] The extremely high pressures in these underground reservoirs indicate that they are leaktight, which make them ideal for storage purposes. Fluid pressures in the sands in these abnormal reservoirs are 2000 to 7000 psi higher than in adjacent aquifers. The shale surrounding the sands evidently is so thick and impermeable that it provides a most nearly perfect seal. There are some 47 of these reservoirs on the Gulf Coast that have abnormally high pressures (below 8000 ft the pressure gradient from the surface is 0.7 to 0.80 psi/ft, or 2000 to 5000 psi higher than normal for the depth).

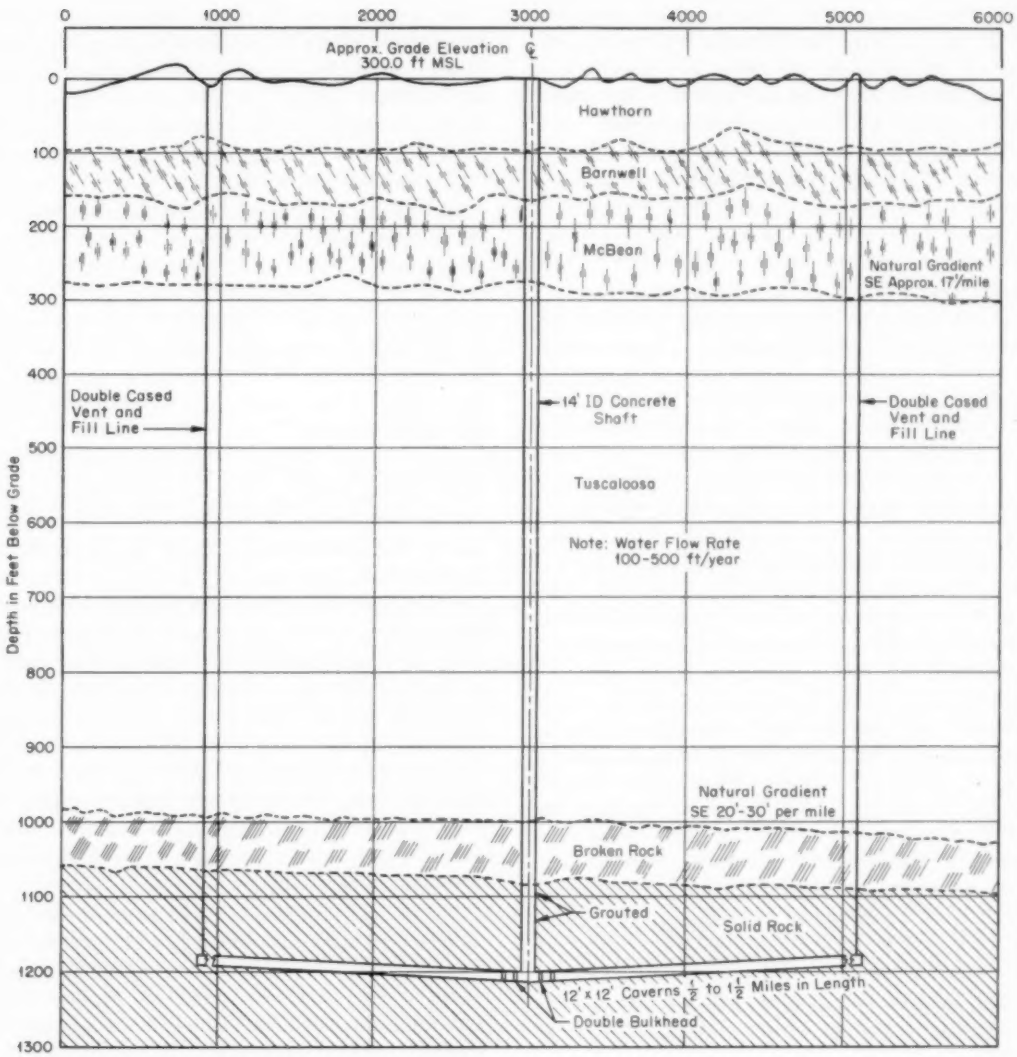

Fig. IV-5 Schematic drawing of proposed Savannah River mine caverns.[3]

Recovery of Fission-Product Isotopes

Effective Mar. 20, 1962, AEC sharply reduced[31] the prices of Cs^{137} and Sr^{90}. The price reductions have been made possible through new processes and increased production capacity at Commission facilities in Richland, Wash., and Oak Ridge, Tenn. The Commission plans to separate and purify megacurie quantities of Sr^{90} and Cs^{137} to assure their ready availability.[6] New prices for Cs^{137} are 50 per cent lower than the former prices. The new Sr^{90} prices are about one-fifth of the old prices.

Wischow and Horner at ORNL have summarized the flow-sheet tests and the process chemistry studies in the development of a solvent-extraction flow sheet for the recovery of Sr^{90} and mixed rare-earth fission products from adjusted Purex 1WW waste solution by D2EHPA (di-2-ethylhexyl phosphoric acid) in Amsco 125-82 TBP (tributyl phosphate).[10,16] In

this process the first-cycle feed is prepared by adding tartrate and caustic to the waste solution to complex the iron and adjust the *p*H. Strontium and rare earths are coextracted with D2EHPA-TBP-Amsco and stripped with nitric acid in the first cycle and then are isolated as concentrated product solutions by processing through additional solvent-extraction cycles. If four cycles are used, the strontium concentration (20 g/liter) is a factor of 70 greater than that of the original waste.

Satisfactory product recoveries and physical operation were demonstrated in bench-scale batch and continuous countercurrent tests with simulated feed solutions. Decontamination factors and ultimate product purity were not demonstrated absolutely since facilities were not available for operation on a sufficiently high-activity-level feed. Equipment operation was satisfactory with pulsed columns, mixer-settlers, or a combination of these devices for the separate operations. It is planned to test this flow sheet in miniature mixer-settler equipment with actual Purex-plant high-activity-level feed.

ORNL is also studying the recovery of strontium and rare earths by ion exchange following a head-end double precipitation step.[1,17] The effect of high flow rates, 15 ml/min (linear velocity 3 cm/min), was tested on the sorption and elution cycles. This high flow rate was chosen to minimize holdup time from the standpoint of radiation degradation. A pretreated Purex-plant 1WW waste containing less than 10 per cent and about 30 per cent of the original iron and aluminum, respectively, and less than 15 per cent of the original sulfate was passed through a column of Dowex 50W-X8 (20 to 50 mesh).

At these high flow rates, equilibrium was not attained in either the sorption or elution cycles. On the sorption cycle, about 97 per cent of the rare earths was sorbed but only about 40 per cent of the strontium was sorbed. Elution with 29 resin volumes of 0.25*M* monosodium citrate (*p*H 3.6) removed only about 75 per cent of the rare earths and also removed 15 per cent of the sorbed strontium; the 0.13*M* sodium versenate (*p*H 6.0) eluted the remaining strontium and rare earths. Both phases of the elution cycle showed the "tailing off" typical of incomplete and slow reaction. This experiment has shown that slower sorption and elution rates as well as finer mesh resin should be tested.

At Hanford the various Purex-plant waste streams continue to be studied as a source of fission products. Precipitation, ion-exchange, and solvent-extraction processes have been used to develop flow sheets to recover and purify Sr^{90}, Ce^{144}, and Pm^{147} (rare-earth cut), Cs^{137}, and Tc^{99} (reference 1).

Several Hanford papers have become available which describe various aspects of their recently concluded program for the recovery and purification of approximately 1 megacurie of Sr^{90} needed for power sources for thermoelectric power units developed for the AEC by the Martin Company.[17,32,33] The work described in these papers has been extensively reported in previous Reviews.[1]

Some 27,000 curies of radiochemically pure Pm^{147} were obtained in an ion-exchange purification run in the "A" cell of the Hanford High-Level Radiochemistry Facility for an over-all recovery of 80 per cent.[34,35]

The promethium feed material came from the head-end treatment, by peroxyacetate precipitation, of Purex-plant 1WW wastes. The loading of the adsorption columns, filled with Dowex 50W-X12 (50 to 100 mesh) resin in the ammonium cycle, required 33 hr, and breakthrough was reached only at the end of the loading cycle. Elution from these columns was with a 0.015*M* EDTA (ethylene diamine tetraacetic acid) solution, buffered to *p*H 8.80 with ammonium hydroxide.

"Cold" yttrium was used as barrier ion in the elution columns (Dowex 50W-X12 resin) and worked very well. (Thorium or aluminum might also be satisfactorily used as barrier ions. Lead cannot be used since it is reduced by radiation in the presence of EDTA and resin in a manner analogous to that experienced with copper in the Sr^{90} recovery program.)[36] During the elution cycle the columns were heated to 55 to 60°C. Column operation was generally quite smooth, and there was little evidence of resin damage or troublesome gassing. A decrease in the *p*H of the elutriant from 8.80 to 8.60 was found largely to eliminate such gassing as was observed.

A prototype remote packaging process for bulk fission products is being developed at Hanford.[34,37,38] Equipment is being designed, installed, and tested.

The over-all packaging process includes the following steps:[38]

1. Canister filling and thermal stabilization of the product in the canister is performed in a loading station. Process design is based on precipitation of a filterable intermediate compound of the fission product, washing of the precipitate, and slurrying of the intermediate into a filter canister wherein thermal conversion to a stable compound is accomplished. With this system, mechanical handling of dry fission-product material is avoided.

2. The canister containing the stabilized fission product is removed to a capping station where a helium purge is applied, and this is followed by sealing with a mechanical, all-metal closure.

3. A third station completes the encapsulation with a remotely welded closure.

4. Decontamination and leak-detection stations will complete the packaging process.

The physical binding or cementing of the dry bulk fission-product compounds into a consolidated dust-free mass inside the shipping canister offers a means of preventing or minimizing the atmospheric release of the powdery product in the event of a catastrophic accident to the container.[34] Initially, materials are being sought that can be codeposited in the shipping container with the fission-product intermediate, and then vitrified by heating during the normal fission-product calcining step.

Several ceramic mixes have been found that will bond with strontium oxide at or below the anticipated calcination temperature.[37] The simplest binder is a mix of lead oxide and silica. The best bond has been obtained with a frit compound of 11 per cent Li_2O, 22 per cent Na_2O, 11 per cent NaF, 19 per cent Al_2O_3, 9 per cent B_2O_3, and 28 per cent P_2O_5. Ten wt.% of this binder fuses strontium oxide into a glassy melt at about 650°C. No suitable binder has yet been found for cerium oxide.

Strontium peroxide with 10 wt.% lead borosilicate binder was calcined in a full-scale size canister.[38] There was approximately 85 per cent shrinkage of the cake volume, but the cake stuck to the canister wall and the filter stick. Strontium peroxide with 3.5 per cent of a borosilicate-phosphate binder containing no lead showed the same shrinkage, but the cake mostly slumped to the bottom of the can. An incompletely calcined portion stuck to the top of the filter stick. Cerous fluoride (62.5 wt.%) fuses with lithium fluoride (37.5 per cent) at 750°C. Cerium oxide (probably CeO_2) can be fluxed with acid-fluoride mixes. Mixtures of aluminum, sodium and/or lithium fluoride with P_2O_5 or B_2O_3 react with CeO_2 at 650°C or less to give fluid melts that freeze to crystalline solids, but the fluxing mix must be added to 40 per cent of the weight of the cerous oxalate $[Ce_2(C_2O_4)_3 \cdot 10\ H_2O]$ intermediate.

References

1. *Reactor Fuel Processing*, 5(2): (April 1962).
2. *Major Activities in the Atomic Energy Programs, January–December 1961*, U. S. Government Printing Office, Washington, January 1962.
3. Atomic Energy Research for 1961 in Life and Physical Sciences, Reactor Development, and Waste Management, A Special Report of the United States Atomic Energy Commission, December 1961.
4. J. R. Pohlman and M. M. Lemcoe, Strength Tests of Prototype Sea Disposal Containers for Radioactive Wastes (Final Report), USAEC Report TID-13942, Southwest Research Institute, San Antonio, Tex., Oct. 20, 1961.
5. *Reactor Fuel Processing*, 3(4): (October 1960).
6. *Reactor Fuel Processing*, 4(4): (October 1961).
7. T. F. Lomenick and K. E. Cowser, Status Report on Evaluation of Solid Waste Disposal at ORNL: II, USAEC Report ORNL-3182, Oak Ridge National Laboratory, Feb. 7, 1962.
8. Oak Ridge National Laboratory, Chemical Technology Division, Unit Operations Section Monthly Progress Report for February 1961, USAEC Report CF-61-2-65, p. 8, July 28, 1961.
9. Oak Ridge National Laboratory, Chemical Technology Division, Chemical Development Section B, Quarterly Progress Report, USAEC Report ORNL-TM-81, p. 40, Jan. 26, 1962.
10. *Reactor Fuel Processing*, 5(1): 51 (January 1962).
11. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Report for October and November 1961, USAEC Report ORNL-TM-133, Oak Ridge National Laboratory, Mar. 13, 1962.
12. R. R. Holcomb and J. T. Roberts, Low Level Waste Treatment by Ion Exchange, II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin, USAEC Report ORNL-TM-5, Oak Ridge National Laboratory, Sept. 25, 1961.
13. J. R. Bower (Ed.), Chemical Processing Technology Quarterly Progress Report, April–June 1961, USAEC Report IDO-14567, p. 27, Phillips Petroleum Co., Nov. 10, 1961.
14. E. R. Irish (Ed.), Quarterly Progress Report on Research and Development Activities, Fixation of Radioactive Residues, July–September 1961, USAEC Report HW-71374, Hanford Atomic Products Operation, Oct. 13, 1961.

15. E. R. Irish (Ed.), Quarterly Progress Report on Research and Development Activities, Fixation of Radioactive Residues, October–December 1961, USAEC Report HW-72324, Hanford Atomic Products Operation, Jan. 15, 1962.
16. R. P. Wischow and D. E. Horner, Recovery of Strontium and Rare Earths from Purex Wastes by Solvent Extraction, USAEC Report ORNL-3204, Oak Ridge National Laboratory, Jan. 29, 1962.
17. L. A. Bray et al., The Recovery and Purification of Multi-Kilocurie Quantities of Fission Product Strontium by Cation Exchange, USAEC Report HW-70998, Hanford Atomic Products Operation, Sept. 8, 1961.
18. D. R. Anderson and D. W. Rhodes, Stainless Steel Wastes: III. Laboratory Studies of the Rate of Removal of Stainless Steel Ions by Mercury Cathode Electrolysis, USAEC Report IDO-14570, Phillips Petroleum Co., Feb. 12, 1962.
19. J. R. Bower (Ed.), Chemical Processing Technology Quarterly Progress Report, October–December 1960, USAEC Report IDO-14553, p. 49, Phillips Petroleum Co., May 15, 1961.
20. J. R. Bower (Ed.), Chemical Processing Technology Quarterly Progress Report, January–March 1961, USAEC Report IDO-14560, p. 63, Phillips Petroleum Co., Aug. 18, 1961.
21. G. Rey, Entrainment from a Submerged Combustion Evaporator, USAEC Report HW-64290, Hanford Atomic Products Operation, 1958.
22. G. Rey, Entrainment from a Submerged Combustion Evaporator, *A.I.Ch.E. Journal*, 7(2): 299 (June 1961).
23. E. R. Irish (Ed.), Quarterly Progress Report on Research and Development Activities, Fixation of Radioactive Residues, April–June, 1961, USAEC Report HW-70517, p. 20, Hanford Atomic Products Operation, July 15, 1961.
24. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for August and September 1961, USAEC Report ORNL-TM-49, p. 7, Oak Ridge National Laboratory, Nov. 29, 1961.
25. F. L. Culler, Jr., Chemical Technology Division Monthly Report for February 1962, USAEC Report ORNL-TM-151, p. 7, Oak Ridge National Laboratory, Mar. 2, 1962.
26. C. W. Hancher and J. C. Suddath, Pot Calcination of Simulated Radioactive Waste with Continuous Evaporation, USAEC Report ORNL-TM-117, p. 9, Oak Ridge National Laboratory, Dec. 26, 1961.
27. H. W. Godbee and W. E. Clark, The Use of Phosphite and Hypophosphite To Fix Ruthenium from High-Activity Wastes in Solid Media, USAEC Report ORNL-TM-125, Oak Ridge National Laboratory, Jan. 30, 1962.
28. J. J. Perona, Optimum Fill Volumes in Pot Calcination of Radioactive Wastes, USAEC Report ORNL-TM-59, Oak Ridge National Laboratory, Nov. 17, 1961.
29. D. G. Jacobs, Cesium Exchange Properties of Vermiculite, *Nuclear Sci. and Eng.*, 12: 285–292 (1962).
30. D. L. Katz, Liquid-Waste Storage in Abnormal-Pressure Reservoirs, *Nucleonics*, 20(4): 71 (April 1962).
31. AEC Reduces Prices of Useful Fission Products, AEC Press Release E-86, Mar. 20, 1962.
32. W. W. Schulz et al., Solvent Extraction Recovery and Purification of Strontium-90, paper prepared for presentation at American Chemical Society's National Meeting, Washington, March 1962.
33. C. R. Cooley and G. L. Richardson, Hanford Atomic Products Operation, Jan. 4, 1962. (Unpublished)
34. W. H. Reas, Chemical Research and Development Operation Monthly Report, November 1961, USAEC Report HW-71921C, p. C-6, Hanford Atomic Products Operation, Dec. 15, 1961. (Classified)
35. W. H. Reas, Chemical Research and Development Operation Monthly Report, October 1961, USAEC Report HW-71535C, p. C-4, Hanford Atomic Products Operation, Nov. 15, 1961. (Classified)
36. *Reactor Fuel Processing*, 4(3): 55 (July 1961).
37. W. H. Reas, Chemical Research and Development Operation Monthly Report, December 1961, USAEC Report HW-72142C, p. C-7, Hanford Atomic Products Operation, Jan. 15, 1962. (Classified)
38. W. H. Reas, Chemical Research and Development Operation Monthly Report, January 1962, USAEC Report HW-72590C, p. C-7, Hanford Atomic Products Operation, Feb. 15, 1962. (Classified)

Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Preparation of Uranium Dioxide

In a detailed review of the actinide oxides, Roberts[1] specifically emphasizes the uranium-oxygen system. Of particular importance in his review is the completely referenced section on the structures of various oxide systems.

Reduction of Uranium Trioxide

In the fluid-bed production of uranium trioxide, a concentrated uranyl nitrate solution is injected under pressure through a nozzle into a bed of uranium trioxide at 315°C. Workers at Harwell[2] have observed that the reduction to uranium dioxide of fluid-bed uranium trioxide with hydrogen proceeds via a $UO_{2.6}$ intermediate phase. Since the reaction between the uranium dioxide product and hydrogen fluoride to produce uranium tetrafluoride does not proceed readily to completion, several means were investigated for producing an active grade of uranium dioxide from fluid-bed uranium trioxide. The following methods were considered:

1. Thermal decomposition of uranium trioxide to U_3O_8 followed by reduction to uranium dioxide
2. Direct reduction of uranium trioxide to uranium dioxide followed by reoxidation to U_3O_8 and reduction to uranium dioxide
3. Conversion of uranium trioxide to $UO_3 \cdot {}^4/_5H_2O$ or $UO_3 \cdot 2H_2O$ followed by dehydration and reduction

Method 1 effects no activation of the uranium dioxide product. Method 2 produces a highly reactive form of uranium dioxide by physical disintegration of particles. (Further details on this activation technique were described in a previous Review.[3]) In method 3 the conversion of uranium trioxide to the dihydrate gives rise to a reactive form of uranium dioxide regardless of the reduction conditions. The reactivity of uranium dioxide prepared from $UO_3 \cdot {}^4/_5H_2O$ is critically dependent on reduction temperature. Preparation of $UO_3 \cdot 2H_2O$ was achieved by hydration of uranium trioxide particles in water at 20°C. Heating of gamma UO_3 in steam at 120°C produced $UO_3 \cdot {}^4/_5H_2O$.

Conditions that determine activation or deactivation of uranium dioxide have been studied in detail by Dell and Wheeler.[2] For a uranium dioxide particle to be reactive toward hydrofluorination, it is most important that the particle should contain sufficient porosity to accommodate the expansion in crystal volume which occurs during hydrofluorination. Other factors that facilitate hydrofluorination are high surface area and small aggregates of uranium dioxide microcrystallites within the particle.

Electrolytic Reduction of Uranyl Chloride

In the electrolytic uranium dioxide process for recovering purified uranium from ore concentrates, the procedure adopted has been to form uranyl chloride, together with other associated chlorides and oxychlorides, by direct chlorination of the concentrate suspended in a sodium chloride–potassium chloride eutectic. The uranium dioxide recovered electrolytically from such melts contains an appreciable quantity of impurities, especially the rare earths. To produce an acceptably pure grade of uranium dioxide, further refining procedures are required. A process involving successive electrolytic purification stages was described in a previous Review.[4]

A modification of the electrolytic uranium dioxide process has been reported by Gibson and Avery.[5] The essential feature of the purification step involves a special electrolytic puri-

fication of the melt to remove soluble impurities without incurring loss of uranium. Process conditions for this step were established in a silica cell that was 3 in. in diameter and 10 in. deep. The uranium ore concentrate, suspended in an equimolar sodium chloride–potassium chloride melt, is completely chlorinated with chlorine gas in the presence of graphite at a melt temperature of 850°C. Aeration of the melt oxidizes the uranium tetrachloride to uranyl chloride. Precipitation of uranium dioxide is effected by injection of hydrogen into the melt. Uranium dioxide particles collect at the bottom of the cell, thus leaving the soluble impurities in the supernatant zone available for removal by electrolysis.

Electrolytic purification of the melt is conducted in a reducing atmosphere of hydrogen to ensure that iron and other metallic impurities are in the lowest valence state and to suppress any formation of uranyl chloride during electrolysis. The electrolysis is carried out at a potential of 3 volts between a graphite anode and a molybdenum cathode. During electrolysis the current constantly decreases owing to the decrease in concentration of iron and other chlorides. It was observed that the cathode deposit retains a considerable quantity of melt when the deposit is removed from the cell. The uranium is recovered from this deposit by leaching the soluble impurities, leaving an insoluble uranium dioxide residue which may be recycled through a hydrometallurgical process. This purification step consistently removed from the electrolyte more than 90 per cent of the iron and associated impurities.

Conversion of the insoluble uranium dioxide to uranyl chloride is effected by injection of chlorine into the agitated melt. Electrolytic recovery of purified uranium dioxide is carried out using graphite electrodes with a potential of from 1.0 to 1.9 volts. It was observed that the first deposit of uranium dioxide carries with it a greater burden of impurities than material subsequently deposited. The impurity levels of iron and rare earths consistently were below 20 ppm in several demonstration tests.

Only half of the total uranium in the melt is recovered as uranium dioxide. The remainder is recycled in the sodium chloride–potassium chloride electrolyte; a constant inventory of uranium is maintained in the melt.

Of major concern in the production of electrolytic uranium dioxide is the fact that a uranium oxide product containing an oxygen-to-uranium ratio greater than 2 has frequently been observed. Wilks[6] has investigated the mechanism of the electrolytic reaction to determine the reason for the formation of U_4O_9 and UO_{2+x} crystals at the cathode. Investigations were performed in an electrolyte of equimolar sodium chloride–potassium chloride eutectic containing from 3.7 to 5.7 wt.% uranyl chloride. Tests were made using a carbon anode and a platinum cathode at a melt temperature of 850°C.

It was observed during electrolysis of uranyl chloride that chlorine, carbon dioxide, and a small quantity of carbon monoxide were evolved at the carbon anode. The molar ratio of carbon dioxide to carbon monoxide varied from 14 at the start of the electrolysis to 2 at the end. This observation may be explained by the carbon reduction of uranyl chloride at the anode to produce uranium tetrachloride. U(IV) oxychloride ($UOCl_2$) also may be formed by the reaction between uranium dioxide and uranium tetrafluoride. An over-all reaction is suggested:

$$6UO_2Cl_2 + 3C \rightarrow UO_2 + 5UOCl_2 + Cl_2 + CO + 2CO_2$$

Further evidence for this anode reaction was the formation of significant deposits of uranium dioxide on the carbon anode. Similar deposits of UO_{2+x} crystals were obtained when stoichiometric uranium dioxide was used as the anode.

A possible source of oxygen in the uranium dioxide product is the formation of U_3O_8 by the thermal decomposition of uranyl chloride in the eutectic. Wilks[6] suggested that the thermal decomposition proceeds by a two-stage reaction involving the formation of $U_3O_8^{2+}$ ions and U(IV) oxychloride. It is postulated that a second reaction takes place between $U_3O_8^{2+}$ ions and the uranium tetrachloride produced by reduction of uranyl chloride at the carbon anode. The reaction product, UO_2Cl, produces UO_2^+ ions during electrolysis, and the presence of these ions in the melt may lead to the formation of U_4O_9 or UO_{2+x} crystals on the cathode.

It is suggested that the formation of UO_{2+x} crystals at the cathode may be eliminated by conducting the electrolysis at a much lower temperature, thereby reducing the thermal decomposition of uranyl chloride. The use of a lithium chloride–potassium chloride eutectic (m.p. 335°C) or a potassium chloride–lead chloride eutectic (m.p. 411°C) might prove

successful. Workers at Hanford Atomic Products Operation (HAPO)[7,8] have studied both eutectic systems, and have prepared uranium dioxide crystals with an oxygen-to-uranium ratio below 2.005. Large (4 g) single crystals were prepared at 550°C in a lead chloride–potassium chloride eutectic.[7] Impurity levels in the crystalline product as low as 20 ppm lead and 10 ppm potassium have been achieved. The prime requisite for the growth of large uranium dioxide crystals of stoichiometric composition appears to be the maintenance of a dry, oxygen-free system. This is achieved by operating the electrolytic cell under a chlorine or hydrogen chloride atmosphere.

Studies of the mechanism of uranium dioxide crystal growth from sodium chloride–potassium chloride systems have indicated that the presence of oxygen affects the crystal habit of the uranium dioxide product. By operating in a thoroughly dry system, dense spheres of uranium dioxide up to 1 cm in diameter may be produced.[9] These spheres have a highly polished appearance and a bulk density of 10.76.

Measurements[8] of capacitance as a function of potential have shown that the electroreduction of uranyl chloride to uranium dioxide in the sodium chloride–potassium chloride system does not proceed by a direct two-electron transfer. Data indicate that a soluble U(V) species exists as an intermediate in the reduction. The mechanism of the reduction is discussed in Sec. III.

Preparation of U(IV) Nitrate Solutions

Considerable interest has been shown recently in the use of U(IV) solutions as reducing agents in the solvent-extraction separation and recovery of plutonium from uranium. Ferrous sulfamate is now employed as a reductant for plutonium, and, although it is a satisfactory agent, its use results in a significant increase in the volume of wastes generated. A considerable saving in storage costs would be realized if ferrous sulfamate were replaced by a reductant that did not contribute to the waste volume.

Ondrejcin[10] has described a simple method for the preparation of U(IV) in nitric acid solution at a yield of 98 per cent. The procedure involves the reduction of U(VI) in 1*M* sulfuric acid with granulated zinc. The U(IV) product is precipitated from solution as the hydrated oxide ($UO_2 \cdot 2H_2O$) by the addition of either sodium or ammonium hydroxide. The hydrated oxide is dissolved in 1*M* nitric acid containing 0.02*M* hydrazine as a holding reductant. U(IV) nitrate solutions were prepared at a maximum concentration of 100 g/liter with a U(VI) content of less than 2 per cent. The U(IV) nitrate solutions were reasonably stable when stored in opaque containers; the decrease in U(IV) content was approximately 0.5 per cent per day.

Several methods for preparing U(IV) nitrate solutions have been investigated on a laboratory scale by H. Katz.[11] Of several methods considered, the precipitation and decomposition of uranyl sulfide to uranium dioxide followed by dissolution in nitric acid appeared most promising. Uranyl sulfide is precipitated by the addition of 1.4*M* uranyl nitrate to 50 per cent excess of an ammonium sulfide solution. The mixture is digested for 90 min at 40°C to decompose uranyl sulfide to uranium dioxide and sulfur. The solids are recovered by filtration and dissolved in 4*M* nitric acid at 60°C. Katz does not recommend the use of an oxidation inhibitor during dissolution of uranium dioxide in nitric acid. A 1-hr dissolution yields a solution containing 83 g of uranium per liter with a U(IV) content of 71 per cent.

All attempts to isolate U(IV) nitrates from aqueous solution have been unsuccessful because of complete conversion of the U(IV) nitrates to uranyl compounds. Bagnall et al.[12] describe the preparation of several complex salts of U(IV) nitrate. A method for preparing cesium hexanitratouranate (IV), $Cs_2U(NO_3)_6$, is described.

A technique for producing halide- and sulfate-free uranous oxalate has been reported by Phillips et al.[13] The method involves the electrolytic reduction of uranyl formate and subsequent precipitation of uranous oxalate with oxalic acid. The reduction was accomplished in a mercury cell with a graphite-rod or platinum-wire anode.

Production of Uranium Tetrafluoride by Reduction of Uranium Hexafluoride

The reduction of uranium hexafluoride by hydrogen is a technique that has been extensively

developed for producing uranium tetrafluoride from uranium hexafluoride.[14] The use of trichloroethylene as an alternative reducing agent has been studied at the Oak Ridge Gaseous Diffusion Plant. A report describing a pilot plant for the reduction of uranium hexafluoride to uranium tetrafluoride with trichloroethylene was declassified last year.[15] The process was studied at three different temperatures and corresponding phase conditions: (1) liquid trichloroethylene at 22°C, (2) liquid trichloroethylene near the boiling point at 82°C, and (3) vapor-phase reaction at 232°C. In both liquid processes the uranium hexafluoride diluted with nitrogen was fed through several ports in the wall of a 16-ft spray tower. Liquid trichloroethylene was introduced through a spray nozzle located at the top of the tower. Both systems proved to be unsatisfactory because of continuous plugging of the uranium hexafluoride feed nozzles, the presence of U(VI) in the product, and the difficulty of recovering the solid product.

It was found that vapor-phase reduction at 232°C produced a low-density product (0.2 to 1.6 g/cm^3) that contained only a small quantity of U(VI). Sintering the uranium tetrafluoride product in a hydrogen fluoride atmosphere increased the density to approximately 3 g/cm^3. The product particle size was 99 per cent less than 5 μ. This product showed a tendency to agglomerate. Approximately 50 per cent of the solid product was collected in the reactor. The remaining solids were recovered efficiently from the off-gas stream with a combination of an electrostatic precipitator and a series of sintered-metal filters. The reduction reaction was essentially complete; the effluent gas contained less than 1 ppm uranium hexafluoride.

Workers at Eldorado Mining and Refining, Ltd.,[16] have initiated studies on the hydrogen reduction of uranium hexafluoride to uranium tetrafluoride by means of a process similar to that developed at Oak Ridge.[14] Process variables have been studied in a 1½-in.-diameter Inconel tube at wall temperatures of 650 and 760°C. High-density uranium tetrafluoride product (3.5 g/cm^3) was obtained by operation with an excess of hydrogen of about 25 per cent. Slag formation on the reactor wall was significantly decreased by increasing the production rate from 3 to 7.5 lb/hr. At the lower rate, slag accumulation on the reactor wall eventually necessitated equipment shutdown.

Galkin and associates[17] have recently compared several methods of reducing uranium hexafluoride with specific emphasis on the factors that affect the purity and density of the uranium tetrafluoride product. Among the processes reviewed were the reduction with hydrogen chloride, hydrogen, ammonia, trichloroethylene, and carbon tetrachloride. Galkin et al.[18] have also reported the results of a study on the kinetics of solution of uranium hexafluoride in organic solvents.

The interaction of uranium hexafluoride and ammonia vapor at low temperatures has been studied by Galkin et al.[19] In the temperature range of 100 to 200°C, the reaction proceeds with the formation of ammonium pentafluorouranate (IV), NH_4UF_5. At lower temperatures the reduction terminated with the formation of uranium pentafluoride. A detailed study of the reaction of gaseous uranium hexafluoride with solid uranium tetrafluoride in the temperature range of 20 to 200°C has been reported by Nguyen.[20] Specific emphasis is devoted to the study of the kinetics of the various reactions observed.

Production of Plutonium Metal

The standard feed for the production of plutonium metal by the peroxide route is a dilute solution of plutonium in nitric acid from the Purex solvent-extraction process. This feed stream contains as impurities some residual fission products and uranium. A complete description of this production method has been published.[21] The sequence of major operations is as follows: cation exchange, for concentration and purification of Purex feed, precipitation of plutonium peroxide, conversion to plutonium tetrafluoride, and reduction to metal. This process has been employed successfully by Du Pont at the Savannah River Plant, although several changes in the operations have been introduced recently.

Concentration by Cation Exchange

At Savannah River[21] a cation-exchange operation based on the Pu(III) system is the first step in the preparation of plutonium metal. At Hanford an anion-exchange process based on

Pu(IV) nitrate complexes is used (see page 69 of this issue). Certain advantages favor the use of the Pu(III) system over Pu(IV) in the exchange. The advantages are as follows: (1) no further adjustment of feed is required since Pu(III) is the product from the Purex solvent-extraction step, (2) the sulfate decontamination step to remove uranium and fission products from the resin would complex Pu(IV) with high loss, (3) capacity of the resin is greater with Pu(III), and (4) the experience with Pu(III) has shown that minimum time cycles and higher plutonium concentrations in the eluate are obtained.

The exchange units are small glass columns containing fixed beds of Dowex 50W resin. The dilute plutonium feed (0.2 to 6 g/cm^3) flows down through the resin column until a desired load of plutonium has been sorbed. The Pu(III) is stabilized in the feed by 0.05*M* hydroxylamine. A dilute sulfuric acid wash (0.25*M* H_2SO_4) removes the sorbed uranium and fission products. The bulk of the plutonium is removed by an eluting solution that contains 5*M* nitric acid and 0.3*M* sulfamic acid. The eluate is divided into fractions depending on the plutonium content. A rich portion is taken as the product fraction, and the fore and tailing fractions are recycled.

Precipitation of Plutonium Peroxide

The precipitation of Pu(IV) peroxide with hydrogen peroxide is a standard method of isolating plutonium from solution. This technique provides excellent decontamination from cationic impurities. The chemistry of the precipitation of Pu(IV) peroxide from nitric acid solutions is complex; two different phases of the solid peroxide may be formed during the oxidation-reduction process. A colloidal face-centered cubic form of peroxide is precipitated from nitric acid solutions below 2*M* in acidity. At higher acidities a hexagonal variety is formed as a dense, crystalline precipitate. The fact that the plutonium in the feed solution is present initially as Pu(III) is thought to aid the precipitation of the crystalline phase, since oxidation to Pu(IV) by hydrogen peroxide is not instantaneous. The lower Pu(IV) concentration seems to aid the formation of larger crystals, which are readily recovered by filtration.

Hydrogen peroxide is added slowly to the plutonium concentrate until the solution is 2*M* in peroxide. Sufficient agitation is provided to prevent the acidity in any region in the vessel from falling below 2*M* and thereby prevent the formation of the colloidal form of plutonium peroxide. Additional hydrogen peroxide is added to the slurry to provide eight times the stoichiometric requirement. The slurry is filtered under vacuum, and the filter cake is washed with refrigerated, dilute (2 per cent) hydrogen peroxide. Precipitation yields[21] have been consistently 99.7 per cent.

Dry, room-temperature air is passed through the filter cake for 2.5 hr, and then dry, warm (55°C) air is passed through for 2 hr. The final moisture content of the cake is reduced to about 0.2 g of water per gram of plutonium, which is a desirable level for feed to the subsequent hydrofluorination step.

The large excess of hydrogen peroxide (about 4*M*) in the filtrate and wash solution is destroyed by heating the solution at 50°C for 45 min; the last traces of peroxide are destroyed by heating briefly at 90°C.

Hydrofluorination and Reduction to Metal

Plutonium peroxide is converted[21] to plutonium tetrafluoride by reaction with hydrogen fluoride gas at temperatures up to 600°C. The tetrafluoride is then reduced with metallic calcium in an induction furnace. The molten plutonium metal separates from the slag and solidifies as a button in the bottom of the magnesia crucible.

The over-all efficiency of both the hydrofluorination and reduction steps appears to be greatly affected by the composition of the peroxide cake. Experience has shown that the sulfate and moisture content of the plutonium peroxide must be controlled properly. The presence of sulfate in the peroxide lowers the bulk density of the final tetrafluoride and thereby decreases the reduction batch size. Also, the time cycle for hydrofluorination is greatly lengthened when the sulfate concentration in the peroxide precipitation feed stream exceeds 0.02*M*. Moisture content of the dried peroxide cake must be controlled between 0.2 and 0.35 g of water per gram of plutonium, or difficulties may occur at the onset of the hydrofluorination step. Material drier than this frequently reacts violently with hydrogen fluoride, and solids are expelled from the boat or furnace. Cakes having a moisture content above this range often de-

compose to a foam that boils out of the container. Moist peroxide also results in a low-density tetrafluoride product.

Calcium alone (no iodine booster) can be used to reduce plutonium tetrafluoride to metal above a certain batch size that is determined by the thermal properties of the equipment. An iodine booster is employed in the reduction of smaller batches or of incompletely converted tetrafluoride. The use of iodine causes various complications and corrosion problems. During the reduction, iodine converts into a cement the magnesium oxide packing sand that holds the crucible in place within the steel pressure vessel. The fused material (magnesium oxide sand, crucible, slag, and metal button) is difficult to remove from the steel container.

One of the major drawbacks associated with the plutonium peroxide–plutonium tetrafluoride process is the considerable corrosion that results from the presence of gross quantities of moisture liberated during hydrofluorination of peroxide. This corrosion appears in the furnace, boats, and off-gas system. Another drawback is the necessity of neutralizing the off-gas, which is a problem associated with any process involving the use of hydrogen fluoride.

Precipitation of Plutonium Trifluoride and Reduction to Metal

Savannah River Laboratory recently began using a process based on the precipitation and reduction of plutonium trifluoride.[22] The stated incentive for changing to the trifluoride process was the elimination of the hydrofluorination step in the peroxide route which had presented many serious corrosion problems. Plutonium trifluoride is precipitated directly from the cation-exchange concentrate by the addition of hydrofluoric acid. The trifluoride is crystalline and can be made in a very large particle size. Since it binds no water, the solid is easily dried to the anhydrous salt. The solubility of plutonium trifluoride is sufficiently low so that the filtrate may be discarded with no necessity for plutonium recovery. Certain disadvantages, however, have been observed with the trifluoride process. These include lower yields in the bomb reduction step and lower decontamination from such elements as iron and aluminum.

The concentrated plutonium solution is fed with the proper quantity of hydrofluoric acid into an initial precipitation vessel made of glass. The resulting slurry overflows into an agitated slab tank of polyethylene, where additional hydrofluoric acid is added. The feed line to the precipitator is monitored continuously for plutonium content by a gamma absorptometer that utilizes an americium source. The tank is critically safe in the event of agitator failure and the resulting accumulation of precipitate from one run on the bottom. A periscope has been installed for internal inspection of the tank so that, if precipitate accumulates during a run, it may be removed prior to the next run. This will avoid inadvertent accumulation of precipitate from several runs on the bottom of the tank.

The performance of the trifluoride precipitation depends, in part, on the relative concentrations of nitric and hydrofluoric acids. Crystal growth is enhanced at conditions of moderate solubility or high nitric-to-hydrofluoric acid ratios. Low plutonium losses are obtained at low nitric-to-hydrofluoric acid ratios. Favorable results have been obtained in the first precipitation stage at a nitric acid-to-hydrofluoric acid ratio of 6 and above, with a nitric acid strength of $3M$ to $5M$. A final ratio of 3 or less gives adequately low losses (0.05 to 0.1 per cent) in the second stage. The presence of strong nitric acid in the initial feed from the cation-exchange columns oxidizes the Pu(III) to Pu(IV) slowly, even with sulfamic acid present. In order to ensure low plutonium losses during precipitation and to provide good filtration characteristics of the precipitate, it is necessary to add ascorbic acid, which is a good specific reducing agent for Pu(IV) in strong nitric acid.

It is possible to obtain a very insoluble precipitate from a Pu(III) nitrate feed containing appreciable Pu(IV) if potassium bifluoride is used as the precipitant. Since most of the plutonium is in the trivalent state, the bulk of the precipitate is plutonium trifluoride, and the Pu(IV) is precipitated as the very insoluble double salt, $KPuF_5$. Unfortunately, as the quantity of Pu(IV) in the feed is increased, the bulk density of the precipitate decreases and the filtration time increases. Addition of ascorbic acid to the feed reduces Pu(IV) to Pu(III); all the plutonium then precipitates as the trifluoride with potassium bifluoride as the precipitant. This modification has not yet been adapted to the trifluoride process.

Over-all decontamination of the plutonium trifluoride precipitation step is less than with peroxide or oxalate precipitation. Not all of the elements that form fluoride complexes remain in the filtrate; when present in low concentrations in the feed, several elements, such as uranium, aluminum, and zirconium, are carried appreciably (30 to 100 per cent) by the cake. As a result the abundance of these specific contaminants in the feed must be regulated more closely than when peroxide or oxalate precipitation is used.

Plutonium trifluoride is highly resistant to oxidation during and after precipitation as long as the precipitate is kept slurried in the supernatant solution, which contains excess hydroxylamine and ascorbic acid.[23] However, when the trifluoride is permitted to settle in the supernatant solution in layers more than 1 cm thick, the reductants that are occluded within the settled trifluoride are soon depleted and oxidation is initiated. Studies show that efficient agitation in the precipitator vessel is the most important factor in avoiding oxidation. No satisfactory antioxidant has been found that prevents oxidation of the precipitate in the absence of efficient mixing.

Plutonium trifluoride slurry is filtered on a batch basis in shallow filter boats made of platinum and Teflon.[24] The precipitate is dried in the same boats by passing dry air through at 80 to 100°C. The filter cake is transferred to a second filter boat having similar dimensions and given a high-temperature cycle to complete the drying and eliminate volatile impurities. A variety of different cycles may be used, and the compound may be reduced to metal with anhydrous plutonium trifluoride, plutonium tetrafluoride, or a mixture of plutonium tetrafluoride and plutonium dioxide.

Plutonium trifluoride reduction feed is prepared by heating the dried cake for 1.5 hr at 600°C in an inert-gas atmosphere. Reduction is made with calcium metal in the presence of an iodine booster. Approximately 0.6 to 0.8 mole of iodine per mole of plutonium is required to provide the additional heat required during reduction.

Plutonium trifluoride can be converted[24] readily to the tetrafluoride by exposure to hydrogen fluoride gas and oxygen at 400 to 600°C for 1 to 2 hr. Since the tetrafluoride provides a higher heat of reaction during reduction, it can be reduced by calcium without an iodine booster. Reduction yield, as in the case of trifluoride reduction, is greater than 99 per cent. This approach to the reduction step possesses an inherent advantage in the elimination of iodine. The major objection to this approach is the operation of a hydrofluorination furnace, which requires additional supply facilities and introduces problems associated with equipment corrosion and off-gas neutralization.

The reduction operation at Savannah River[24] uses as a feed a mixture of plutonium tetrafluoride and plutonium dioxide prepared by calcining the plutonium trifluoride filter cake in an oxygen atmosphere at 300 to 600°C. Owing to a high heat of reaction, the fluoride-oxide mixture may be reduced without the use of an iodine booster. However, the large amount of calcium oxide in the slag interferes with coalescence of the plutonium metal, and the reduction yield is only 95 to 97 per cent. This reduction cycle has the advantages of avoiding the use of iodine and avoiding the problems associated with the hydrofluorination step. Since in all reduction cycles both recovery and recycle of plutonium from skulls and crucibles are required, no additional problems are associated with the recovery of this plutonium.

Recovery of Plutonium from Scrap Materials

Plutonium Recovery from Reduction Residues

A semicontinuous process has been developed at Savannah River for the recovery of plutonium from residues produced in the calcium reduction process.[25] The reduction operation generates about 2.5 kg of solid residue for each kilogram of plutonium reduced. The residue contains magnesium oxide sand and crucible, calcium fluoride, calcium oxide, excess calcium metal, and a mixture of plutonium fluorides, oxide, and metal. From 2 to 5 per cent of the plutonium charged in the reduction process appears in the residue.

The first step in the recovery process is the dissolution of the residue in nitric acid. The current procedure at Savannah River incorporates batchwise dissolution in a stainless-steel vessel that does not possess critically safe dimensions. Although this procedure has been used successfully, it has these disadvantages:

a long time cycle of dissolution is required, severe corrosion of the dissolver occurs, and extremely careful control of operations is necessary to avoid criticality incidents.

A semicontinuous dissolution process, employing a Teflon-lined dissolver of critically favorable dimensions, has been demonstrated as a favorable alternative to the batch dissolver in laboratory tests.[25] The most satisfactory procedure consisted of a two-step dissolution in which the residue was treated first with hot 10*M* nitric acid and then with hot 10*M* nitric acid–0.5*M* aluminum nitrate solution. In this procedure 99 per cent of the plutonium and about 95 per cent of the residue were dissolved with a solution-to-solid ratio of about 15 ml/g.

Plutonium was recovered from the unfiltered dissolver solution in greater than 99 per cent yield by sorption on a series of three small, agitated beds of anion-exchange resin. Since plutonium may oxidize to the Pu(VI) state during dissolution, valence adjustment was required prior to contact with the resin. Two valence-adjustment schemes were tried: (1) addition of 0.1*M* sodium nitrite and (2) addition of 0.05*M* ferrous sulfamate followed by heating at 55°C. Since sorption of plutonium was most favorable from feed solutions adjusted with ferrous sulfamate, this procedure was adopted in the recovery process. Plutonium loss during the washing of the loaded resin with 8*M* nitric acid was less than 0.01 per cent per bed volume of wash solution. Sorbed plutonium was eluted with 0.3*M* nitric acid to produce a dilute (approximately 1.8 g of plutonium per liter) product solution. This product was particularly well suited for recycle to a primary solvent-extraction system.

A continuous, critically safe dissolver was developed at Hanford[26] for slag and crucible dissolution. The residues are produced by bomb reductions of plutonium tetrafluoride with calcium. Iodine is added as a booster and as an aid in the breaking away of slag and other materials from the metal button. Initial demonstration tests were conducted using simulated feed materials in a 5-in.-diameter by 10-ft-high dissolver that was made of AISI type 309SNb stainless steel. Slag and crucibles were crushed and packaged into steel cans prior to dissolution. Dissolver feed was a solution of 8*M* nitric acid and 0.17*M* aluminum nitrate. Agitation of the reacting mixture was effected by a steam sparge. In the absence of sparging, the sand and crucible chips settled to the bottom of the dissolver into a tightly packed, impervious agglomerate. In spite of fast reactions and small liquid surface area, entrainment and foaming did not occur in demonstration tests. The off-gas line to the condenser was sufficiently above the product overflow line to prevent liquid from entering the condenser. The dissolver throughput rate was limited by the duration of the vigorous, consecutive reactions that dissolved both the can containing the slag and crucible material and the fine solids within the can. The dissolver product solution contained 4.8*M* nitric acid and a small quantity of suspended solids identified as oxides of magnesium and silicon.

A series of laboratory-scale tests at HAPO has successfully demonstrated the continuous dissolver process, using plutonium-bearing slag and crucible residues generated from actual plant operation.[27] It was observed that the vigorous reaction which occurred during initial phases of dissolution of each solids charge produced large quantities of foam. Formation of a considerable foam volume, which would result in boilover from the dissolver, could be obviated by charging smaller batches more frequently. In all the experimental runs, a residual solids heel formed in the dissolver. Since heel dissolution is slow, periodic cleaning of the dissolver will be required in order to maintain a low heel volume.

Some concern was given to the formation of iodate ions from the small quantity of calcium iodide present in the slag material, since plutonium iodate has a very low solubility. It was determined that a 27.5 g/liter iodate concentration is required to precipitate plutonium iodate from the dissolver. Iodate concentration in demonstration tests was uniformly less than 5 g/liter, and precipitation of plutonium values was not encountered.

Plutonium is recovered from the dissolver solution by solvent extraction with a 20 vol.% solution of tributyl phosphate (TBP) in carbon tetrachloride. The dissolver solution is prepared for solvent-extraction recovery by adjustment with aluminum nitrate enneahydrate [$Al(NO_3)_3 \cdot 9H_2O$]. Four stages of extraction were required to reduce the plutonium concentration in the aqueous feed from 2 to 0.03 g/liter. The presence of up to 0.08*M* titanium or 0.3*M* sulfate did not decrease the extractability of plutonium.

Recovery of Plutonium from Uranium and Thorium Alloys

A process is being developed at HAPO for recovery of plutonium from scrap generated from plutonium-uranium and plutonium-thorium materials.[28] The process is based on dissolution or leaching of the scrap in a nitric acid–hydrofluoric acid mixture to prepare a solution suitable for plutonium recovery by solvent extraction. Crushed or steam-oxidized scrap is dissolved in a 13*M* nitric acid–0.5*M* hydrofluoric acid mixture. A feed for solvent-extraction columns is prepared by adjusting the dissolver product solution with the addition of a 2.2*M* aluminum nitrate solution and a solution containing ferrous ammonium sulfate, sulfamic acid, and nitric acid.

A single-cycle solvent-extraction system containing three extraction columns is used to prepare a plutonium solution essentially free of uranium and thorium. A solvent containing 20 per cent TBP in carbon tetrachloride is used. The extraction process is designed primarily to achieve a high decontamination factor for plutonium in the thorium-uranium product. By recycling the thorium-uranium stream back as an intermediate scrub solution, a product containing less than 10 parts plutonium per billion parts uranium may be prepared.

Plutonium Chemistry and Technology

Ion Exchange

Various ion-exchange processes have been developed and adopted for the final purification and concentration of plutonium nitrate solutions. Such processes have been applied to plutonium product streams at both Savannah River and HAPO. Ion-exchange processes also have been adopted for the processing of plutonium metallurgical scrap. At Savannah River[25] a quadrivalent-plutonium anion-exchange process has been developed to recover plutonium wastes in fixed-bed columns. A preliminary appraisal of a process for the separation of plutonium from uranium, iron, and fission products using an anion-exchange resin, Dowex 1, in 10*M* nitric acid solution has been made by Allison and Hart at Chalk River.[29]

In a recent paper Oberg and Swift[30] described the continuous anion-exchange process developed at HAPO to complete the decontamination of plutonium from traces of fission products and associated metallic ions. Plutonium is one of the few elements that can form anionic nitrate complexes which can be sorbed readily on anion-exchange resins from nitrate solutions. In nitric acid systems the distribution coefficient increases with increasing nitrate concentration up to 7.3*M* nitric acid and then decreases gradually at higher acidities. It is believed that plutonium is sorbed as the $Pu(NO_3)_6^{2-}$ complex and that, as the acid concentration is raised to 7.3*M*, the increasing nitrate activity promotes formation of the complex. At higher acid concentrations, acidic complexes are formed.

Pu(IV) in mineral acids will disproportionate to some degree, forming Pu(III) and Pu(VI) ions, and a technique for adjusting the valence of plutonium may be required for efficient operation of an anion-exchange process. The valence of plutonium in a Pu(IV)-Pu(VI)–nitric acid system may be adjusted to 4 by reduction with ferrous sulfamate.[31] The nitric acid concentration must be between 2*M* and 6*M* to avoid plutonium disproportionation or sulfamate precipitation. The procedure requires the stoichiometric addition of ferrous sulfamate; excess ferrous ions reduce Pu(VI) to Pu(III).

The rate of plutonium sorption on anion-exchange resins is markedly increased with increasing temperature, with a maximum sorption occurring between 60 and 70°C. Loading tests[30] indicated that both Dowex 1 X-4 (50 to 100 mesh) and Permutit SK (20 to 50 mesh) were superior to other resins for this application. Of the resins examined for radiation damage, Permutit SK was found most resistant; when a sample was irradiated to 3.4×10^8 r, the exchange capacity decreased 35 per cent, but cross-linkage reduction was small.

The Hanford plutonium-ion-exchange unit[30] consists of sorption and elution columns connected by a downcomer that permits flow of resin from the top of the sorption column to the bottom of the elution column. By supplying air pressure to the system, it is possible to move the resin intermittently through the column circuit. The exchange columns operate by alternately introducing feed and pumping resin. The over-all time cycle for the unit is about

5 min. The feed stream to the columns consists of the plutonium product stream from a solvent-extraction process. The feed is made 6*M* in nitric acid and heated to 70°C before entering the sorption column. A 6*M* nitric acid scrub stream is employed to wash occluded fission products and other foreign ions from the column. This waste stream is recycled to a solvent-extraction process for plutonium recovery. Elution of plutonium is achieved in a 1*M* nitric acid solution. The product stream is concentrated in a thermosiphon concentrator to about 250 g of plutonium per liter.

During laboratory tests[30] it was determined that considerable improvement in the decontamination factor could be achieved by the addition of fluoride ion to the feed solution. A decontamination factor of from 10 to 25 was achieved with a fluoride-ion concentration of 0.005*M*; previously a decontamination factor of only 3 to 5 was obtained. The recovery efficiency for plutonium under normal processing conditions was high, since only about 0.5 per cent of the plutonium that was processed was lost from the sorption column.

Preparation of Plutonium Tetrafluoride from Plutonium Dioxide

Fusion of plutonium oxide in ammonium bifluoride is being considered at HAPO as a method of recovery of plutonium from plutonium dioxide wastes.[32] This technique may also have application for plutonium recovery from incinerator ash and from plutonium metal and skulls which have previously been converted to plutonium dioxide by steam oxidation or controlled burning.

Ammonium bifluoride fusion of plutonium dioxide proceeds according to the following equation:

$$2PuO_2 + 5NH_4FHF \rightarrow 2PuF_4 \cdot NH_4F + 3NH_3 + 4H_2O$$

The double salt product breaks down under heat to form solid plutonium tetrafluoride and volatile ammonium fluoride. This reduction has been studied by Maly et al.[33] on a microthermobalance. It appears that the initial product is a hydrated double salt that decomposes in the temperature range 160 to 200°C, yielding anhydrous NH_4PuF_5. At 250 to 270°C this material decomposes to solid plutonium tetrafluoride.

The HAPO process[32] involves mixing plutonium dioxide with ammonium bifluoride in a 1:8 mole ratio and heating the mixture in a stainless-steel vessel for 2 hr at 200°C. Process conditions were established using 35-g batches of plutonium dioxide. An argon purge is employed throughout the entire heating cycle to remove volatile gases from the system. After the heating cycle is completed, the molten salt product is poured directly into a hot (100°C) 2*M* solution of aluminum nitrate. The plutonium salt readily dissolves, and the resulting solution is amenable to direct solvent-extraction processing.

No plutonium-bearing residues were found in the laboratory tests; the average plutonium recovery was 95 per cent.

The plutonium tetrafluoride resulting from the fusion process could be reduced to metal directly if the purity of the salt were satisfactory. However, the plutonium tetrafluoride contains ammonium bifluoride, and methods for its removal have not been explored.

References

1. L. E. J. Roberts, The Actinide Oxides, *Quart. Revs. (London)*, 15(4): 442–460 (1961).
2. R. M. Dell and V. J. Wheeler, Atomic Energy Research Establishment, Harwell, England, October 1960. (Unpublished)
3. *Reactor Fuel Processing*, 5(2): (April 1962).
4. *Reactor Fuel Processing*, 5(1): 66–67 (January 1962).
5. A. R. Gibson and R. G. Avery, Atomic Energy Research Establishment, Harwell, England, 1960. (Unpublished)
6. R. S. Wilks, A Study of the Mechanism of the Electrolysis of UO_2Cl_2 in Molten NaCl-KCl Eutectic, Atomic Energy Research Establishment, Harwell, to be published.
7. W. H. Reas, Chemical Research and Development Operation Monthly Report, October 1961, USAEC Report HW-71535C, Hanford Atomic Products Operation, Nov. 15, 1961. (Classified)
8. W. H. Reas, Chemical Research and Development Operation Monthly Report, December 1961, USAEC Report HW-72142C, Hanford Atomic Products Operation, Jan. 15, 1962. (Classified)
9. L. P. Bupp, Chemical Research and Development Operation Monthly Report, February 1961, USAEC Report HW-68712C, Hanford Atomic Products Operation, Mar. 15, 1961. (Classified)
10. R. S. Ondrejcin, Preparation of Uranium(IV) Nitrate Solutions, USAEC Report DP-602, Savannah River Laboratory, July 1961.

11. H. Katz, Some Methods of Preparing Tetravalent Uranium Solutions, USAEC Report BNL-691, Brookhaven National Laboratory, September 1961.
12. K. W. Bagnall et al., The Uranium(IV) Nitrates, *J. Chem. Soc.*, pp. 4060–4063 (September 1961).
13. L. R. Phillips et al., Preparation of Uranous Oxalate, USAEC Report Y-1308, Union Carbide Nuclear Co., Y-12 Plant, July 7, 1959.
14. *Reactor Fuel Processing*, 2(1): 49 (January 1959).
15. J. E. Baker et al., A Pilot Plant for the Reduction of Uranium Hexafluoride to Uranium Tetrafluoride with Trichloroethylene, USAEC Report K-1271 (Del.), Union Carbide Nuclear Co., Oak Ridge Gaseous Diffusion Plant, May 31, 1956 (declassified July 26, 1961).
16. Eldorado Mining and Refining, Ltd., Research and Development Div., Monthly Reports (of) Development: for June 1961, Report NP-10438, Oct. 2, 1961; for September 1961, Report NP-10914, 1961.
17. N. P. Galkin et al., Methods of Reducing Uranium Hexafluoride, *Soviet J. At. Energy*, 10(2): 143–149 (November 1961). Translated by Consultants Bureau from *At. Energ.*, 10(2): 149–155 (February 1961).
18. N. P. Galkin et al., A Study of the Properties of Uranium Hexafluoride in Organic Solvents, *Soviet J. At. Energy*, 10(2): 138–142 (November 1961). Translated by Consultants Bureau from *At. Energ.*, 10(2): 143–148 (February 1961).
19. N. P. Galkin et al., Interaction of Uranium Hexafluoride with Ammonia, *Soviet J. At. Energy*, 8(6): 444–448 (July 1961). Translated by Consultants Bureau from *At. Energ.*, 8(6): 530–534 (June 1960).
20. Hoang-Nghi Nguyen, Contribution to the Study of the Intermediate Fluorides of Uranium, French Report CEA-1976, 1961.
21. E. W. Mainland et al., Production of Plutonium Metal, *Ind. Eng. Chem.*, 53(9): 685–694 (September 1961).
22. G. A. Burney and F. W. Tober, Precipitation of Plutonium Trifluoride, paper presented at the American Chemical Society Meeting, Washington, March 1962.
23. J. A. Porter, The Stability of PuF_3 in the Trifluoride Precipitation Process, USAEC Report DP-621, Savannah River Laboratory, August 1961.
24. D. A. Orth, Plutonium Metal from the Trifluoride, paper presented at the American Chemical Society Meeting, Washington, March 1962.
25. E. K. Dukes and W. E. Prout, Savannah River Laboratory, June 1961. (Unpublished)
26. H. T. Blaine, Continuous Slag and Crucible Dissolver, USAEC Report HW-68630, Hanford Atomic Products Operation, February 1961.
27. H. W. Crocker, Continuous Dissolution of Plutonium-Bearing Slag and Crucible Residues, USAEC Report HW-69415, Hanford Atomic Products Operation, June 1961.
28. L. E. Bruns, Flowsheet for Separation of Plutonium from Thorium and Uranium, USAEC Report HW-67674, Hanford Atomic Products Operation, Dec. 7, 1960 (declassified Jan. 4, 1961).
29. G. M. Allison and R. G. Hart, The Separation of Plutonium by Anion Exchange in 10*M* Nitric Acid Solution, Part 1: Preliminary Investigation, Canadian Report PDB-86(AECL-1372), May 1953, reissued in September 1961.
30. G. C. Oberg and W. H. Swift, Continuous Anion Exchange Processing of Plutonium, paper prepared for presentation at meeting of American Institute of Chemical Engineers, Los Angeles, Feb. 4–7, 1962.
31. M. H. Campbell, Selective Reduction of Plutonium(VI) to Plutonium(IV) in a Plutonium(IV-VI) Nitric Acid Solution, USAEC Report HW-68003 (Rev.), Hanford Atomic Products Operation, February 1961.
32. H. W. Crocker, Ammonium Bifluoride Fusion of Ignited Plutonium Dioxide, USAEC Report HW-68655, Hanford Atomic Products Operation, Feb. 24, 1961. (Classified)
33. Ia. Maly et al., Reaction of Plutonium Dioxide with Ammonium Hydrogen Fluoride in the Absence of Water, USAEC Report AEC-tr-4787, Nov. 14, 1961. Translated from *Radiokhimiya*, 3(2): 195–198 (1961).

LEGAL NOTICE

This document was prepared under the sponsorship of the U. S. Atomic Energy Commission. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

NUCLEAR SCIENCE ABSTRACTS

The U. S. Atomic Energy Commission, Division of Technical Information, publishes *Nuclear Science Abstracts (NSA)*, a semimonthly journal containing abstracts of the literature of nuclear science and engineering.

NSA covers (1) research reports of the U. S. Atomic Energy Commission and its contractors; (2) research reports of government agencies, universities, and industrial research organizations on a world-wide basis; and (3) translations, patents, books, and articles appearing in technical and scientific journals.

Complete indexes covering subject, author, source, and report number are included in each issue. These are cumulated quarterly, semiannually, and annually providing a detailed and convenient key to the literature.

Availability of *NSA*

SALE *NSA* is available on subscription from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., at $22.00 per year for the semimonthly abstract issues and $15.00 per year for the four cumulated-index issues. Subscriptions are postpaid within the United States, Canada, Mexico, and all Central and South American countries, except Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Subscribers in these Central and South American countries, and in all other countries throughout the world, should remit $27.50 per year for subscriptions to semimonthly abstract issues and $17.50 per year for the four cumulated-index issues.

EXCHANGE *NSA* is also available on an exchange basis to universities, research institutions, industrial firms, and publishers of scientific information. Inquiries should be directed to the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tennessee.

TECHNICAL PROGRESS REVIEWS may be purchased from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. for $2.00 per year for each subscription or for $0.55 per issue. The use of the coupon below will facilitate the handling of your order.

POSTAGE AND REMITTANCE: Postpaid within the United States, Canada, Mexico, and all Central and South American countries except as hereinafter noted. Add $0.50 per year, or $0.15 per single issue, for postage to all other countries, including Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Payment should be by check, money order, or document coupons, and MUST accompany order. Remittances from foreign countries should be made by international money order, or draft on an American bank, payable to the Superintendent of Documents, or by UNESCO book coupons.

order form

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON 25, D. C.

Enclosed:
document coupons ☐ check ☐ money order ☐

Charge to Superintendent of Documents No._____

Please send a one-year subscription to

☐ REACTOR MATERIALS
☐ POWER REACTOR TECHNOLOGY
☐ NUCLEAR SAFETY
☐ REACTOR FUEL PROCESSING

(Each subscription $2.00 a year; $0.55 per issue.)

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON 25, D. C.

(Print clearly)

Name_____

Street_____

City_____ Zone____ State_____